SUPERCRITICAL WATER OXIDATION OF NITROGEN-CONTAINING ORGANIC COMPOUNDS: PROCESS ENHANCEMENT USING ISOPROPYL ALCOHOL

By

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ABSTRACT

The research demonstrated in this thesis aimed to investigate the efficiency and viability of supercritical water oxidation (SCWO) technology in treating diluted N,N-dimethylformamide (DMF), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and ammonia containing model wastewaters. In addition to the hazard and widely usage of these compounds in industry, their selection was also since they have different degrees of refractoriness and are not easy to be effectively destroyed by conventional methods. Also, ammonia is a common unwanted intermediate that produced during treating nitrogenous wastewaters.

A laboratory-scale SCWO system (continuous plug flow reactor) was operated to obtain necessary data to investigate the destruction of the selected compounds at certain operating conditions. The obtained data was also used to study the oxidation kinetics of DMF and DBU. Besides, investigating the typical operating conditions, Isopropyl Alcohol (IPA) was used as a novel approach to enhance the destruction efficiency of this method in treating DMF, DBU and ammonia. This also included investigating the effect of IPA on ammonia reduction as an intermediate during the oxidation of DMF and DBU.

The studied operating parameters were temperature, initial organic concentration, oxidant ratio, initial IPA concentration and residence time. Hydrolysis experiments for DMF and DBU were conducted in the absence of oxygen and at 400^{o}C where their results showed no remarkable decomposition. Results from the SCWO of DMF, DBU and ammonia showed that the temperature was the most influential variable on their destruction. Near complete TOC removal was obtained during DMF oxidation at 525^{o}C and 250 bar, while ammonia was the major reaction intermediate. With DBU oxidation, also near complete TOC conversion was achieved at525^{o}C and 250 bar. The SCWO showed its higher destruction efficiency to treat DBU even

though it has more complex molecular structure compared to DMF. On the other hand, the temperature range of 400-550^{o}C was not enough to achieve a significant destruction for ammonia due to its refractoriness even though it has a simple molecular structure.

Initial organic concentrations showed a positive effect on the destruction of DMF and DBU. Also, using different oxidant ratios improved the removal of DMF, DBU and ammonia. The effects of both variables had less extent of that observed during investigating the temperature.

Using IPA showed a significant enhancement in the destruction of DMF, DBU and ammonia when used as a novel approach. For instance, a TOC removal of 99.4% and 99.2% was achieved for DMF and DBU respectively at 525^{o}C and 250 bar when IPA was added. Also, maximum total nitrogen removal of 97% was obtained at 550^{o}C and 250 bar.

Also, results from kinetic study showed the presence of IPA caused a significant reduction in the activation energy of treated compounds where the values were 21.9 and 25.7 kJ/mol for DMF and DBU, respectively. Kinetic analysis also showed that oxygen has an influence and with oxygen order of 0.38 and 0.32 for DMF and DBU respectively, which agrees with the literature.

Moreover, using IPA in a hydrothermal process (SCWO) showed other features. For instance, the presence of IPA reduces the needed operating temperatures, which can lower the cost of this technology and also enable to treat refractory compounds at less severe conditions. Generally, excess heat generated from exothermic reaction can be recovered to pre-heat the feed or to produce electricity power, which ultimately enhance the economic feasibility of this method. Combining the destruction efficiency and economic features of the SCWO would enhance its reliability further as an alternative treatment technology for wastewaters.

To my big family

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

BOD	Biological oxygen demand
BPR	Back pressure regulator
COD	Chemical oxygen demand
DBU	1,8-Diazabicyclo [5.4.0] undec-7-ene
DMA	Dimethylamine
DMF	Dimethylformamide
GC	Gas chromatograph
HPLC	High-performance liquid chromatography
IC	Inorganic carbon
MA	Methylamine
NIST	Nation institute for standards and technology
NO_x	Nitrous oxides
OH	Hydroxyl radical
PFR	Plug flow reactor
RSD	Relative standard deviation
SCW	Supercritical water
SCWO	Supercritical water oxidation
SO_x	Sulphur oxides
SR	Stoichiometric ratio

SS	Stainless steel
TC	Total carbon
TCD	Thermal conductivity detector
TMA	Trimethylamine
TOC	Total organic carbon
TN	Total nitrogen
TWR	Transpiring wall reactor

Alphabetical Symbols

[Organic]	Organic compound initial concentration (mol/L)
[Oxidant]	Oxidant concentration (mol/L)
$[H_2O]$	Water concentration (mol/L)
A	Pre-exponential factor (s^{-1})
a	Order of reaction with respect to target reactant
b	Order of reaction with respect to oxidant
c	Order of reaction with respect to water
E_A	Activation energy (kJ/mol)
k	Reaction rate constant (s^{-1})
Kw	Ion Product
L	Reactor length
P_c	Critical pressure

r	Rate of reaction
R	Universal gas constant (8.314 J/mol.K)
Re	Reynolds Number
T	Reaction temperature (K)
T_c	Critical temperature
TOC_{DBU}	TOC of DBU
TOC_{DMF}	TOC of DMF
V_r	Reactor volume
X_{DBU}	Conversion of DBU
X_{DMF}	Conversion of DMF
X_{TOC}	Conversion of TOC

Greek Symbols

ε	Static dielectric constant
μ	Dynamic viscosity
ρ	Fluid density
τ	Reactor residence time

CHAPTER 1- INTRODUCTION

1.1 Background and Motivation

There is a necessity to meet the growing global demand of clean water. In addition, the annual production of large amounts of wastewaters from different industrial sources affects this demand and causes environmental challenges to humans, soil, plants and atmosphere. Therefore, it is essential to develop efficient treatment methods in order to minimise this environmental risk by removing the hazardous wastes and thus increasing re-usable clean water. Such methods must meet the strict disposal regulations that have been established by governments. Environmental agencies have established the disposal standards for numerous waste types. For example, the urban wastewater directive (91/271/EEC) stated that the typical discharge values for total nitrogen (TN), chemical oxygen demand (COD) and the biological oxygen demand (BOD) need to be 10 mgL^{-1}, 125 mgL^{-1} and 25mgL^{-1}, respectively.

To reach the goal there are a number of available disposal methods (no destruction) such as landfilling, deep-well injection and land based disposal. However, none of them has become an ideal solution to destroy the hazardous organics in wastewaters.

More reliable and advanced treatment methods have been developed and used that aim to destroy the harmful organic pollutants using different approaches such as biological and chemical (oxidation) methods. However, every one of these methods has its own drawbacks based on wastewater type, composition, needed degree of removal in addition to process economics (this topic is thoroughly discussed in Chapter 2). For instance, incineration is able to achieve complete destruction for wastewaters, but has some drawbacks such as using very high temperatures (up to 1100^{o}C) and generating NO_x. Also, it can operate auto-thermally only with high organic

concentrations (e.g. 40wt% and above), otherwise external fuel is needed. Also, the growing public concerns restrict its usage.

Since several industrial sources produce a wide range of hazardous materials with lower concentrations (0-20wt %), this makes using incineration inconvenient in which a new alternative technology is needed.

Supercritical Water Oxidation (SCWO) is the most promising and alternative destruction technology that is able to treat a wide range of organic pollutants in wastewaters in enclosed systems. The advantages of this method are based on the emerged thermodynamic properties of supercritical water (SCW) as a unique medium for dissolving both organic compounds and oxidants. SCWO is able to achieve an efficient conversion for organic wastes into final non-harmful products such as CO_2 and water in short reaction times (< 1 min). In addition, it is ideal and efficient to treat low organic concentrations (up to 20wt%) at relatively mild operating temperatures (400-650^{o}C) and without any NOx produced. Also, it's characterised by recovering produced heat that enhances its economics. SCWO systems can be designed as stationary or mobile units that can be built close to waste sites. On the other hand, technical challenges such as corrosion and salt precipitation could affect the performance of SCWO.

Nitrogen-containing organic compounds are a general class of hydrocarbons that are non-biodegradable, toxic and abundant in numerous industrial waste effluents (e.g. chemical, pharmaceutical and municipal sources). In general, nitrogen atom has a complex chemistry. Also, the oxidation of such compounds in SCWO generates a refractory intermediate, ammonia, that's highly toxic for aquatic life even at moderate concentrations in which further treatment at harsh operating conditions (e.g. higher than 650^{o}C) is needed to be effectively destroyed. The presence of these compounds in low concentrations (0-20wt%) such as in medical wastes suits also SCWO

capability. Accordingly, it is highly important to destroy such hydrocarbons by SCWO in order to assess this treatment technology.

Therefore, the motivation for this research is to evaluate the performance of SCWO for treating three model pollutants that were selected to represent different classes of nitrogen-containing compounds using co-fuel as a novel approach, in addition to their presence in medical wastes, which is among the interests of our research group. Dimethylformamide (DMF: C_3H_7NO) is relatively a simple aliphatic amide that widely used as a solvent in numerous industries particularly in pharmaceutical synthesis.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU: $C_9H_{16}N_2$) is a complex tertiary amide (hetero-polycyclic) that commonly used as a catalyst in organic and pharmaceutical manufacturing. Ammonia (NH_3) is the most refractory compound that widely used as a raw material for the production of various compounds in numerous industries such as fertilizers, pharmaceutical and cleaning agents. Furthermore, Isopropyl alcohol (IPA: C_3H_8O) as a co-fuel was selected in this work as enhancer to evaluate its effect on the hydrothermal oxidation of selected models compounds. IPA is a secondary alcohol that is widely preferred due to its rapid oxidation and high heating value (i.e. 1830 kJ/mol).

1.2 Aim and Objectives

The overall aim of this research is to investigate the role of IPA to enhance the destruction efficiency of chosen nitrogenous compounds (in aqueous wastewaters) using a lab-scale SCWO tubular reactor at different conditions. In addition, evaluating its effect on the reaction kinetic parameters and operating temperatures. The obtained data from this work could play an important role to improve the viability of SCWO as a promising waste treatment technology via improving

its performance, system design, economics and mitigate its weak points especially at larger scales. Also, this study would provide a SCWO kinetic database for studied nitrogenous compounds. In addition, this would increase the knowledge and understanding of SCW and hydrothermal oxidation reactions.

The core research objectives in this work are to:

a) Study the treatability of SCWO for DMF, DBU and ammonia using a lab-scale continuous flow rector at different conditions. These compounds were selected as they represent different classes of nitrogen-containing compounds. Thus, it would help to establish for a general understanding about SCWO efficiency to treat such pollutants and make a comparative study between more complex class of hetero-cyclic organic other simpler class of nitrogen-containing compounds.
b) Investigate how the presence of co-fuel (Isopropyl alcohol) could enhance the destruction of the selected compounds as a new approach in SCWO process at different operating conditions. This includes identifying the range of process operating conditions that achieve acceptable destruction for the targeted compounds. Also, this includes investigating the effect of adding co-fuel on ammonia as unwanted intermediate from DMF and DBU oxidation.
c) Study hydrothermal oxidation reaction kinetics of DMF and DBU. This included determining kinetic parameters and oxygen order in addition to evaluating the influence of adding co-fuel on activation energy and the possibility to lower the operating temperatures from external heat source that consequently enhances the process economics.

1.3 Thesis Structure

This PhD thesis consists of eight chapters. This chapter covers the background and motivation, aims and the structure layout of this thesis.

Chapter 2 presents a comprehensive literature review on current treatment methods of waste and wastewaters, thermodynamic properties of SCW, SCWO process description and advantages, rector concepts, technical challenges, previous SCWO works on different compounds and wastes, kinetics and mechanisms, energy recovery and finally the status of SCWO commercialization.

Chapter 3 shows the used equipment, materials, procedures and analytical methods used during all experiments.

Chapter 4 discusses the results obtained from the SCWO of DMF at different operating conditions in the presence of IPA compared to non-IPA system in addition to the kinetic analysis.

Chapter 5 discusses the SCWO of DBU at various conditions in the absence of IPA a base study for the SCWO of DBU in the presence of IPA that discussed in Chapter 6. Both Chapters also includes their kinetic studies.

Chapter 7 was dedicated for the SCWO of ammonia in the absence of IPA followed by evaluating the effect of using IPA at different operating conditions.

Finally, Chapter 8 presents the conclusions drawn from the experimental work in this thesis and the recommended further works that are expected to make a positive addition in future.

CHAPTER 2 – LITERATURE SURVEY

This chapter provides an overview of current state-of-the art waste treatment technologies, supercritical water, supercritical water oxidation technology and finally SCWO research that has been undertaken on a wide range of wastes and wastewater.

2.1 Importance of Wastewater and Waste Treatment

Hazardous waste is the waste that has potential threats to human health or the environment during its collection, storage, treatment and disposal. U.S. EPA defines the properties of hazardous waste in terms of ignitability, corrosivity, reactivity, and toxicity. These wastes can be found in different physical states such as gaseous, liquids, or solids. Many hazardous wastes contain a broad range of toxic materials that have serious impact on humans and air, water and land if disposed without proper treatment. In addition, there are carcinogenic pollutants that can get into the food chain through surface- and groundwater supplies. Such wastes can be found in several industrial and municipal waste sources. For instance, these sources include chemical manufacturing, household, pharmaceutical and medical, pesticides, petroleum, explosives, paint & dye, mining, and textile activities and sludge. Effluents from such sources could include a wide range of toxic organics containing halogens, solvents, sulfur and nitrogen, cyanide, PCBs, heavy metals, cutting oils and other aliphatic and aromatic pollutants (Shaw et al., 1991). Moreover, several types of these organic pollutants are non-biodegradable which leads to a persistent impact that lasts for years or decades.

The United Nations Environmental Programme (UNEP) estimated that more than 400 million tons of hazardous wastes are produced universally every year (UNEP, 2016). A hazardous waste is a special type of waste that requires specialized treatment systems.

To treat such wastes in wastewaters regular landfilling is currently available. However, though it's relatively inexpensive, this technique does not provide the ultimate destruction of hazardous components of waste, in which surface- and groundwater could be contaminated. Also, landfill is limited by land availability and facing increasing public concern (Fodor and Klemeš, 2012).

On the other hand, there are several aqueous waste treatment and destruction methods, such as carbon adsorption, biological process (biodegradation), wet air oxidation (WAO) and incineration that considerably cost more than disposal methods, where each method has its own advantages and drawbacks (as discussed in subsequent sections). The selection of the most suitable treatment method for certain wastewater relies on the feasibility of treatment and process economics, in which each method has its own ability depending on the quantity of wastewater, the composition and concentration of organic pollutants in feed streams.

Currently, incineration is a method that can completely destroy hazardous wastes at high temperatures in addition to its ability to recover energy. However, this method releases hazardous flue gases and other particulates from combustion process. Moreover, it has a negative public perception and requires high capital and operating cost.

For these reasons, developing advanced destruction technologies is needed to overcome the effect of such hazardous wastes based on the strict environment standards, which is the issue that has attracted many researchers and companies. The basic aim of efficient waste treatment technologies simply is to completely destroy toxic organic compounds into simpler, non-harmful

and biodegradable final products. For instance, EPA goals is to achieve A destruction of 99.9999% of toxic organic compounds in totally enclosed treatment facilities (Veriansyah and Kim, 2007). European Environmental Agency (EEA) have released pollution control directive that sets disposal standards. For example, the urban wastewater directive (Directive 91/271/EEC) aims to protect the environment from the effects of collection, treatment and disposal from certain industrial sectors and the disposal of sludge. The common recommended release standards for total nitrogen (TN), chemical oxygen demand (COD) and biological oxygen demand (BOD) are 10 mg/L, 125 mg/L and 25 mg/L, respectively. These strict environmental targets would minimise the role of using conventional treatment methods such as physical, biological oxidation in addition to chemical oxidation processes (Veriansyah and Kim, 2007).

2.2 Current Treatment Methods

This section provides an overview on available treatment methods including their advantages and drawbacks. In general, wastewater treatment unit operations can be classified into physical, biological and chemical methods (ESCWA, 2015).

2.2.1 Conventional Methods

Activated carbon adsorption is a physical treatment method that simply adsorbs organic molecules through porous activated carbon and allows for treated water to pass. Activated carbon adsorption treatment method is effective for very dilute aqueous wastes, with an organic content of less than 1wt.%, however, with organic concentration higher than 1wt%, this method becomes economically unfeasible (Veriansyah and Kim, 2007).

A biological method is based on utilizing bacteria and microorganisms to degrade organic and inorganic molecules in wastewater, using the released energy to convert organic carbon into carbon dioxide and clean water. Biological treatment method is effective for very dilute aqueous wastes, organic content less than 1wt.%, however, with organic concentration higher than 1wt%, this method becomes poisoned (Veriansyah and Kim, 2007). Biological oxidation process is widely used but limited to biodegradable compounds that do not contain toxic or inhibitory products for this process (kill bacteria), otherwise, chemical oxidation process is preferred (Cocero, 2001). Also, biological method is limited to certain types of wastes where micro-organisms are existing and some preliminary steps are required. Moreover, it requires long treatment times such as days or weeks and suitable conditions for microbial growth (Fang et al., 1993). In general, this method has lower operating costs compared to other methods.

2.2.2 Chemical Oxidation Methods

Chemical method means adding chemical reagents as oxidants in addition to heat source. These methods are classified to incineration, advanced oxidation processes and hydrothermal oxidation processes.

2.2.2.1 Incineration

Incineration is a thermal waste treatment method that commonly used to treat aqueous wastes, sludge, and solid wastes from different sources, such as industrial and municipal wastes. It was developed during industrial revolution in which the first plant in the UK was built in Nottingham in 1874, then this technology spread to the US and Europe. The incinerator is mainly consists of a furnace that used for waste thermal burning. It combusts organic substances contained in waste materials into flue gas, ash, and heat. Ash is generated by inorganic components of the waste and may take the form of particulates carried by the flue gas. According

to the European Waste Incineration Directive, incineration plants must be designed to reach a temperature of at least 850°C for 2 seconds and with 200% air excess to provide effective treatment for flue gases and toxic organic substances. After combustion the heat from flue gases can be recovered to be utilized. Also, the flue gas is passed through a cleaning system that consists of scrubbers and filters (Fodor and Klemeš, 2012).

Incineration that comes as an alternative for landfilling is able to achieve a complete destruction for a wide range of organic materials. It's able to achieve a 95% reduction in volume and a 80% reduction in mass of materials going to final landfill (DEFRA, 2013). This method is very suitable for the treatment of specific types of wastes such as medical wastes where high temperatures can destroy pathogens and toxins. The medical waste is also characterised by its high calorific value and non-harmful ash is produced. Also, this method is suitable for countries that have a limited land as is the case in Japan.

Moreover, incineration is characterised by energy recovery especially for wastes with high calorific value. After combustion the flue gases are cooled in the super-heaters, in which the produced heat is transferred to generate steam via boilers and then the steam is passed via steam turbines to generate electricity. Also, produced hot steam can be utilized as a heat source for other uses (e.g. hot water for other industrial or domestic applications).

On the other hand, incineration has other drawbacks. The major challenge is the emissions of flue gases and ash. The flue gases may contain toxic dioxins, furans, nitrogen oxides (NO_x), sulfur dioxide, carbon oxides, ash solid particles, heavy metals, and acids. Flue gases must be effectively cleaned of hazardous gases and particulates before disposal. Dioxins and furans are considered to be serious health hazards. Carbon dioxide from combustion is a green-house gas that plays a role in global warming. Solid pollutants are represented by fly ash and bottom ash,

which represents 15–20% of the original waste weight. The fly ash has more health hazards due to the high concentrations of heavy metals as well as small amounts of dioxins and furans, while the bottom ash is a non-hazardous material that can be treated at high temperatures (~1100^{o}C) or safely landfilled or recycled as a construction material. Also, incineration is constrained by the high capital cost compared to other technologies. However, heat recovery can offset its cost. Also, it requires medium to high operating cost and high operating standards.

The negative public perception of incineration is still a limiting factor due to producing large amounts of toxic emissions especially with older facilities. Modern incinerators are supported with more advanced cleaning systems that could effectively reduce flue gas emissions (NRC, 2015). Fine particles (ash) in flue gases can be efficiently removed from by baghouse filters. The next step of the cleaning is the removal of acids and heavy metals from flue gas using scrubbers. Before filtration, with the reaction of lime, sulfur dioxide in flue gas is converted in to gypsum. NO_x (only produced above 815^{o}C) is either reduced by catalytic reduction with ammonia or by a high-temperature reaction with ammonia in the furnace. In addition, newer energy integration technologies have been developed in order to make the process economically viable (Fodor and Klemeš, 2012). However, the drawbacks of incineration currently remain apparent and the views of waste management, such as minimization, reuse, recycle and landfill instead of incineration are still proposed.

More importantly, several manufacturing processes produce dilute wastewaters (1-20wt% organic content) with highly toxic organic compounds which are often non-biodegradable. Examples of dilute wastes include anti-cancer drugs, spent catalysts and chemical warfare agents (Shaw and Dahmen, 2000, Abeln et al., 2001). Incineration is restricted for economic reason for wastes with high organic concentration (> 25 wt% organic content) in addition to the need for high temperatures such as 850-1100^{o}C and with excess air of 100-200% to achieve high

destruction (Veriansyah and Kim, 2007). Others have reported that that incineration becomes inefficient for pollutant concentrations below 40wt% as the high organic concentration produces the required heat for the system otherwise, with lower concentration a supplement fuel is needed (Pinto et al., 2006a).

Therefore, due to the challenges of incineration there is a need to find more advanced oxidation technologies to treat such dilute wastewaters with non-biodegradable organics in enclosed system that is closed to the waste production site to minimize the level of exposure in order to meet the disposal standards.

SCWO is an alternative and a promising treatment technology that has showed its destruction efficiency for several types of aqueous wastes either on academic research or industrial level as will be discussed in this chapter.

2.2.2.2 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs), a set of chemical treatment procedures designed to remove organic materials in wastewater by oxidation using hydroxyl radicals ($OH^{\bullet}$). $OH^{\bullet}$ is a powerful, non-selective oxidant compared to other oxidants (as shown in Table 1). Once produced, the hydroxyl radicals rapidly and aggressively attack virtually all organic compounds. The mechanism in AOPs follows three essential steps, the generation of $OH^{\bullet}$, initial attacks by $OH^{\bullet}$ on target molecules and breaking down to fragments, then chain reaction continues by $OH^{\bullet}$ until ultimate mineralization. AOPs are alternatives to the incineration to treat a wide range of toxic organic wastes. The AOPs follow one of two routes, oxidation with O_2 (if main oxidant) at relatively higher temperatures (always needed to react O_2 with organics). $OH^{\bullet}$ radical then is produced from organic and oxygen reaction, where these radicals un-selectively attack any

organic or water, or by using high energy oxidants such as ozone, H_2O_2 and/or photons that are able to directly decompose to generate high reactive $OH^{\bullet}$ radicals.

Table 1: Relative oxidation power of some oxidizig species (Munter, 2001).

Oxidizing species	Relative oxidation power
Chlorine	1.00
Hypochlorous acid	1.10
Permanganate	1.24
Hydrogen peroxide	1.31
Ozone	1.52
Atomic oxygen	1.78
Hydroxyl radical	2.05
Positively charged hole on titanium dioxide, TiO_2^+	2.35

There are several AOPs methods that generate OH radicals which are classified into non-photochemical and photochemical methods as shown below:

-non-photochemical methods:

- Ozonation at elevated pH (> 8.5)
- Ozone + hydrogen peroxide (O_3/H_2O_2)
- Ozone + catalyst (O_3/CAT)
- Fenton system (H_2O_2/Fe^{2+}): uses Fe^{2+} ions as the catalyst.

-photochemical methods:

- O_3/UV
- H_2O_2/UV
- O_3/H_2O_2/UV
- Photo-Fenton/Fenton-like systems
- Photo catalytic oxidation (UV/TiO_2)

The attack by the OH radical, in the presence of oxygen, initiates complex chain reactions that lead to mineralization of the organic compound. For instance, chlorinated compounds are oxidized to intermediates, such as aldehydes and carboxylic acids and finally to CO_2, H_2O, and the chloride ion. Organic nitrogen in feed is usually oxidized to nitrate or to free N_2, while sulphur is oxidized to the sulphate. AOPs are suitable for destroying dissolved organic

contaminants such as halogenated compounds, aromatics, detergents, pesticides and also to oxidize inorganic contaminants.

Several pilot and large-scale applications of AOPs have been established. Solarchem Environmental Systems is a pioneer company in this field that has more than 50 large-scale installations of UV/O_3, UV/H_2O_2, or O_3/H_2O_2 systems worldwide, treating different contaminants in industrial wastewater, groundwater, and drinking water. In Los Angeles well water is currently being treated by the O_3/H_2O_2 AOP to remove trichloroethylene (TCE) at a scale of 450 m^3/h. Also, O_3/H_2O_2 system has been used for atrazine removal from River Seine water in Paris at a scale of 5000 m^3/h. UV disinfection plants are widely used for drinking water treatment throughout Europe and USA.

Advantages of AOPs:

- AOPs effectively destroy organic compounds in aqueous phase where water is the product of the complete reduction of $OH^{\bullet}$ and without any toxic substances.
- High reactivity and unselectively of $OH^{\bullet}$, allows for $OH^{\bullet}$ to reacts with almost all aqueous pollutants, thus AOPs could be used for many contaminants at the same time.

Disadvantages of AOPs:

- AOPs are characterized by high costs due to the continuous feeding by expensive reagents that needed to maintain the operation.
- Some techniques need pre-treatment of wastewater to guarantee reliable performance. For instance, presence of bicarbonate ions can reduce the concentration of $OH^{\bullet}$ by producing H_2O and much less reactive species.
- AOPs individually unable to handle large amounts of wastewaters; in which AOPs can be applied as a final stage when primary and secondary treatment removed most of contaminants.
- The chemical mechanisms of AOP are still not fully understood.

It is obvious that previously treatment methods have some drawbacks that limit their fully application on wastewater treatment, thus further development is needed for more advanced and efficient methods.

2.3 Introduction to Sub- and Supercritical Water

The basic idea of hydrothermal oxidation processes is the exploitation of elevated temperature and pressure water as a reaction medium. Increasing the temperature and the pressure of water far from those of ambient conditions dramatically changes its physicochemical properties to become a unique reaction medium. The high temperature and pressure water can be classified as subcritical and supercritical water (SCW). Subcritical water has a temperature range of 150-350^{o}C and a maximum pressure of 2-20 MPa, while water becomes supercritical above its critical point which is 374^{o}C and 22.1 MPa (Portela Miguélez et al., 1997, Lee and Park, 1996). Mizuno and co-workers have pointed out that the new features of supercritical water are due to the changes in its density, dielectric constant, ion product, viscosity, diffusivity and solvent ability (Mizuno et al., 2000).

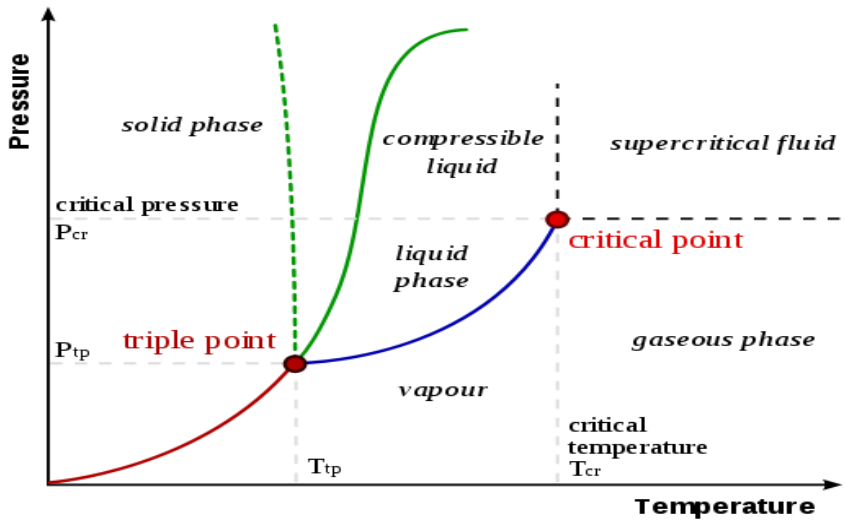


Figure 1: Temperature-pressure diagram of pure substance.

Shaw et al. (1991) reported that as temperature increases mainly above 380^{o}C, water density decreases that result in hydrogen bond breakage where eventually dielectric constant decreases. For example, at the critical point the density of water, 300kg/m^3, which is intermediate between liquid water, 1000kg/m^3, and water vapor, 1kg/m^3 (Cocero, 2001). On the other hand, as pressure increases water vapor becomes denser. Therefore, in supercritical environment the liquid water becomes less dense due to temperature increase and water vapor becomes denser due to pressure increase that results in homogenous mono-phase medium as shown in Figure 1. Thus, water above its critical point is no longer liquid or gas where multi-phase boundary disappears. Williams and Onwudili (2006) have illustrated that vapor and liquid phases become distinguishable and water behaves as a dense gas with removal of any inter-phase mass transport limitations, which increases the diffusivity. The density of water versus the temperature at atmospheric and supercritical pressure of 250 atm is shown in Figure 2 that shows how these variables tune SCW density. Density of water vapor varies greatly with the pressure at a given temperature which keeps medium in mono-phase during reaction (Shaw et al., 1991).

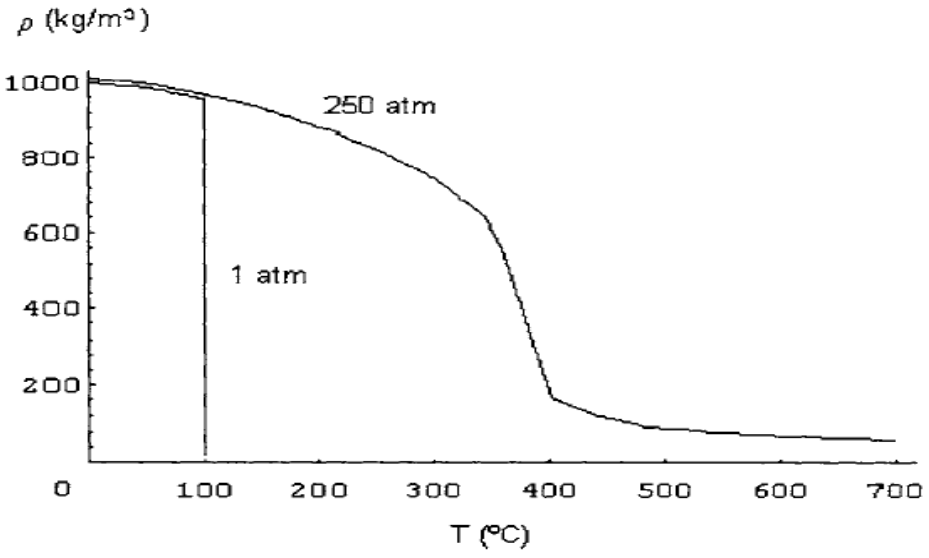


Figure 2: Density of water vs Temperature at 250 atm (Cocero, 2001).

Increasing temperature and pressure lowers dielectric constants of supercritical water compared to ambient water, which results in less and weaker hydrogen bonds that provides uncommon properties for supercritical water. The dielectric constant of SCW is much lower, and the number and persistence of its hydrogen bonds are both diminished, which enhances the solubility of organic compounds in SCW and then rapid and complete reaction occurs (Williams and Onwudili, 2006). For example, water at 500^{o}C (0.1 g/cm^{3}) preserves only 10-14% of its hydrogen bonds that exist for ambient water, while at 400^{o}C (0.5 g/cm^{3}) it preserves around 30-45% (Hoffmann and Conradi, 1997). This is as a results of breakage of hydrogen bonds as temperature and pressure elevated into smaller clusters (Akiya and Savage, 2002).

The static dielectric constant (Ɛ) is an indicator of the polarity of the solvent, where this constant for water decreases with elevating temperature and pressure and as density decreases. For instance, at 300^{o}C with density of 0.75 g/cm^{3} the dielectric constant of water is 21 and becomes 4.1 at 500^{o}C with density of 0.3 g/cm^{3} compared to 78 at ambient conditions (Heger et al., 1980). Others showed that the static dielectric constant decreases from 80 at ambient conditions to around 5-10 in the near-critical region and finally to around 2 at 450^{o}C (Uematsu and Frank, 1980, Cocero, 2001). At these low values of dielectric constant, the high temperature-pressurized water acts as non-polar solvent compared to ambient water (Rebert and Kay, 1959). This results in enhancing the solubility of organics and gases in supercritical water, in which they become completely miscible. The emerged physicochemical properties of Water change its character from a solvent only for ionic species (polar) at ambient conditions to a mono-phase solvent for non-ionic species (non-polar) and gases at supercritical conditions (Brunner, 2009b).

Another factor that is significantly influenced by temperature and pressure is ion product (*Kw*) of water, which is the product of ion concentration in a solution at any time. It increases from ambient conditions until near critical conditions, then decreases at supercritical conditions. For instance, at subcritical conditions the ion product (*Kw*) of water is around 3 orders of magnitude higher than that of ambient water (Akiya and Savage, 2002), where at these conditions it has higher concentrations of H^+ and OH^- ions that is an ideal medium for acid and base catalysed reactions (Marshall and Franck, 1981). By contrast, the (*Kw*) for SCW (at lower densities as < 0.1 g/cm^3) is around tens of orders of magnitude lower than that of ambient water. Therefore, dramatic decrease in (*Kw*) value at more severe conditions, ≥400^{o}C and 24 MPa states the mechanism of oxidation reaction either to be free radical or ionic mechanism, where here free-radical mechanism is dominant at high temperatures and with low density environment. Free radical mechanism is favoured when $Kw << 10^{-14}$ while ionic mechanism dominates when $Kw > 10^{-14}$ (Antal et al., 1987). Brunner (2009b) reported that reactivity of water increases in the neighbourhood of the critical point without or with catalyst. Figure 3 shows the major physical properties of water versus temperature and dielectric constants for some organic solvents.

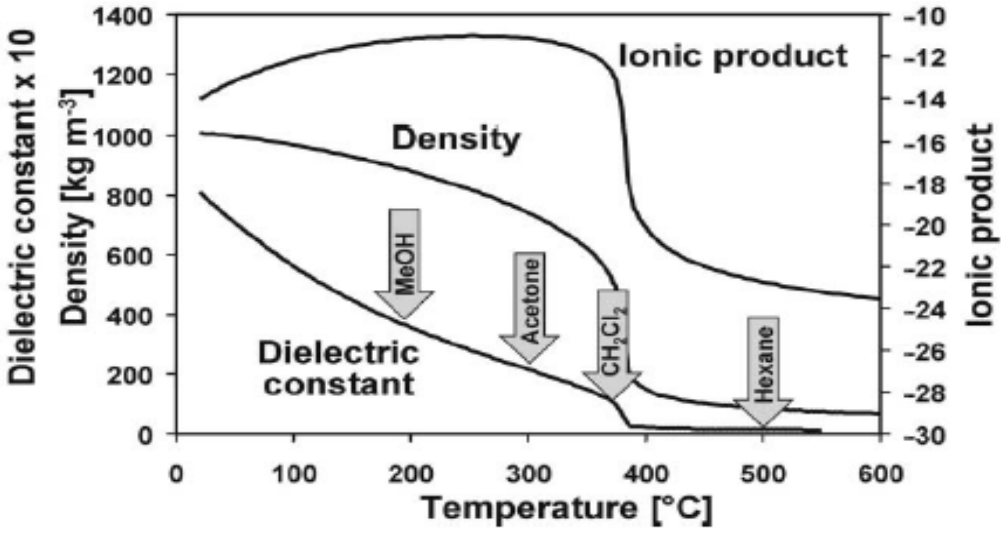


Figure 3: Water physical properties versus temperature at 24 MPa, and Dielectric constants of common organic solvents at room temperature (Kritzer and Dinjus, 2001).

In summary, the emerged new physicochemical properties of water at supercritical conditions establish for the formation of a unique single-phase medium that completely dissolves organic compounds (non-polar) and gases in one medium and without any inter-phase mass and heat transport limitations. Thus, this enhances solubility, diffusivity and then rapid contact and reaction occurs.

2.4 Hydrothermal Oxidation Processes

The concept of hydrothermal oxidation methods is based on the utilization of water as a medium to oxidize unwanted toxic organic materials at both high temperatures and pressures. The interest in the application of hot pressurized (sub) and supercritical water started in the late 70s of last century due to the oil crisis, environmental concerns and the promising investigations of supercritical fluids (Brunner, 2009b). Supercritical fluid technology was developed in 1980s as $scCO_2$ to replace harmful and expensive organic solvents that need further steps to be separated where this medium (CO_2) used later for material extraction, processing and synthesis. The

supercritical water technology has received an interest during the last three decades (since the early 1980s) as a promising alternative to incineration and a further development of wet air oxidation (WAO) process for treating aqueous organic waste effluents (Kritzer and Dinjus, 2001). Elevated temperatures up to 350°C and elevated pressure of 20 MPa are the subcritical conditions of water, which used as in case of WAO. On the other hand, water becomes supercritical fluid above its critical point which is (T_C=374°C and P_C=22.1MPa), and these are the initial supercritical conditions that applied in SCWO. Apart from treatment, oxidation processes have the feature of producing biogas from biomass wastes rather than just burning them as in incineration (Brunner, 2009b).

2.5 Wet Air Oxidation

WAO is a hydrothermal oxidation process that able to decompose aqueous wastes at elevated temperatures and pressures and in the presence of oxidant to smaller and less non-toxic products. Elevated temperatures and pressures enable sub-critical water to enhances the contact between aqueous organic and oxidant in two-phase medium, thus enhances their solubility which facilitates to the reaction. WAO is an efficient method that has emerged as the first developed hydrothermal oxidation process. It is suitable for lower concentration organics compared to incineration. It has shown the ability to treat wastewaters with organic concentrations ranging from 1wt% to 20wt% in enclosed system in addition to its ability to recover energy and inorganics (Veriansyah and Kim, 2007). WAO is operated at temperatures of (150-350°C) and pressures of (2-20MPa) where this pressure maintains reaction in liquefied phase (Veriansyah and Kim, 2007). It is a good alternative to incineration to treat dilute aqueous wastes but has less efficiency to completely destroy some refractory compounds such acetic acid and ammonia

unless catalyst is used. Cocero (2001) has reported that WAO capacity is satisfactory for upgrading the process to the industrial scale, even if it is not sufficient to allow for its effluent emission to the ambient conditions. Kritzer's group has reported that in the WAO process the full removal of the organic materials is seldom achieved and reaction times last up to several hours (Kritzer and Dinjus, 2001). Another study has reported that WAO routinely achieves 70-80% of destruction for organic carbon with longer residence times indicating larger reactor volumes and further treatment are needed (Loppinet-Serani et al., 2010). This is due to the existence of two-phase medium that does not facilitate for full solubility and thus for a complete destruction.

The drawbacks of WAO and previously mentioned conventional methods in addition to the firm disposal standards have encouraged developing more advanced treatment technologies. Therefore, SCWO has been suggested and investigated as an alternative treatment method.

2.6 Supercritical Water Oxidation

2.6.1 Preface

The great role of SCW (above 374^{o}C and 22.1 MPa) as an exclusive medium is the driving force for the application of SCWO for treating aqueous wastes. It has been pointed out that organic compounds and gases such as O_2, N_2, CO, CO_2 are completely miscible in water in near critical and supercritical region (Brunner, 2009b). Thus, SCW is a green medium that facilitates for good contact between organic molecules and oxidant in which a rapid and complete oxidation reaction occurs. SCWO is characterized by short residence times which are due to the effect of increasing temperature on the medium density (lower density vs higher flow rate). For example, researchers have reported that organics in SCWO are rapidly oxidised with high conversions (99.99%) and with residence times of less than one minute (Webley et al., 1991, Schmieder and Abeln, 1999). Another feature of using SCWO is that fewer, simpler (smaller molecular weight

species), non-harmful and biodegradable final products are typically generated compared to former conventional wastewater treatment methods. The typical final products from SCWO treatment are carbon dioxide, water and molecular nitrogen (if the waste stream contains nitrogen content). NO_x and SO_x gases are typical by-products in combustion methods (incineration) but in SCWO they are not exist due to the used lower temperatures that prevent their formation (Veriansyah and Kim, 2007, Cocero, 2001). NO_x only appears at high temperatures as above 850^{o}C. Some have reported that SCWO has the advantage that the outlet aqueous phase and produced gases are safe, no toxic products are ejected to the air and no need for any post treatment (Loppinet-Serani et al., 2010).

SCWO is suitable for lower organic concentrations for the range from 1wt% to 20wt% that incineration unable to treat. Moreover, compared with incineration, SCWO operates at relatively low temperatures in addition to its potential to recover and integrate excess heat that could significantly make this process economically feasible based on the heating value of feed. In the case of feed with high-heating value the SCWO process can be energetically self-sufficient. Cocero et al. (2002) has reported that recovering energy to preheat waste stream and maintain temperatures results in process integration that improves its economic feasibility.

Hydrolysis is an associated reaction in SCWO process, which occurs when organic molecules react with water in the absence of oxygen (Akiya and Savage, 2002). Hydrolysis has been studied by several researchers and has shown that it is a possible route to recover and synthesize useful chemicals from complex polymers (Lee and Gloyna, 1992, Meyer et al., 1995, Holgate et al., 1995, Krämer et al., 1999). For instance, hydrolysis of resins and waste plastics yielded phenol and cresol (Suzuki et al., 1999) in addition to oils (Su et al., 2004, Sugano et al., 2009). Therefore, this proves the flexibility of SCWO technology to achieve efficient destruction or to be used for synthesis based on operating conditions applied. Pyrolysis of organic wastes is

another application in SCWO process as it occurs in the absence of oxidant either in preheater or inside the reactor.

In general, the features of SCWO process can be summarized as below:

- SCW is a green unique solvent and reaction medium that eliminates using harmful organic solvents that require further steps for separation (also more expensive).
- In SCWO process almost all non-polar aqueous organic wastes and gases can be dissolved in one medium, while other organic solvents are unable to do so.
- SCWO achieves a rapid and complete removal with final products of CO_2, N_2 and water, or traces of simple biodegradable by-products that formed from incomplete oxidation.
- SCWO able to treat wastes with lower organic concentrations (< 25wt%) where incineration becomes energetically inefficient to treat.
- Its effluent has no toxic gas emissions as NO_x or dioxins due to using lower temperatures as NO_x appears at higher temperatures (> 700^{o}C).
- Recovering and integrating of oxidation excess heat makes this process economically feasible, as the recovered energy can be used for pre-heating the feed or producing power.
- Using SCWO continuous flow system allows treating large amounts of wastes and also in enclosed system.

2.6.2 Treatment Efficiency

SCWO as the most advanced hydrothermal oxidation technology has shown its efficiency to treat a wide range of toxic and non-biodegradable wastes such as chemical, petrochemical, food and pharmaceutical aqueous wastes under SC conditions even without catalyst usage (Brunner, 2009b). It has attracted attention due to its ability to completely destroy organic compounds in waste streams to yield mainly CO_2 and water in the presence of oxygen (Williams and Onwudili,

2006). Extensive studies have proven that SCWO is an effective and efficient method to treat many organics and toxic wastes, such as PCBs, dioxins, process wastewaters, pharmaceutical waste, sludge, human waste, energetic, dyes and military wastes (Veriansyah and Kim, 2007). For example, it was found that up to 99% destruction of the polycyclic aromatic compounds occurred at supercritical conditions (Brunner, 2009a). Other researchers have showed in a review that several model compounds and industrial wastes were treated by SCWO with destruction greater than 99.9% (Cansell et al., 1998). Aki and Abraham reported that the SCWO of organic waste stream yields destruction efficiency greater than 99.99% at temperatures above 525°C (N.V.K. Aki and Abraham, 1999).

Studies covered general classes of organics from simple to more complex as explained in this chapter. This includes hetero-atom organic compounds that cause challenges such as corrosion and salt formation as in case of halogenated and sulphided compounds. Recently, there is more interest in nitrogenous organic compounds due to complexity of nitrogen chemistry and the refractory nature of ammonia as a common intermediate. In general, the most treated compounds included phenols, ammonia, acids as acetic acid, PCBs, simple compounds like methane, alcohols and formaldehydes. Also, there have been several studies about SCWO reaction mechanisms and pathways, kinetics, engineering challenges, reactor designs and energetics (Cabeza et al., 2014).

However, Williams and Onwudili (2006) reported that the majority of work has been carried out on the SCWO of pure compounds, while real environment pollutants appear as complex mixtures. Also, Cocero et al. (2000a) pointed out that most previous works with N-containing species have been performed from a kinetic point of view, on a laboratory scale and the destruction of some compounds was not always complete. Furthermore, there has been a little success to remove ammonia unless higher temperatures, longer residence times, co-fuels or catalyst used. Svishchev and Plugatyr (2006) pointed out that the detailed understanding of

SCWO reactions is still limited due to lack of systematic experimental data in a wide temperature range and complicated kinetics. Kritzer and Dinjus (2001) added that the lack of experimental data and cost evaluations over long period of time made SCWO has not become a current waste treatment technology at large scale plants. Also, they added that SCWO can become an alternative to incineration in special-limited cases, but not for all types of wastes. In addition, high control measures are needed due to using relatively high pressures and temperatures especially for large scale applications of SCWO.

2.6.3 SCWO Process Description

The lab-scale experimental apparatus is shown in Figure 11 in Chapter 3. The typical SCWO process consists of three major sections; feed preparation and pressurization, reaction, cooling and depressurization. The main features of the SCWO process are shown in Figure 4.

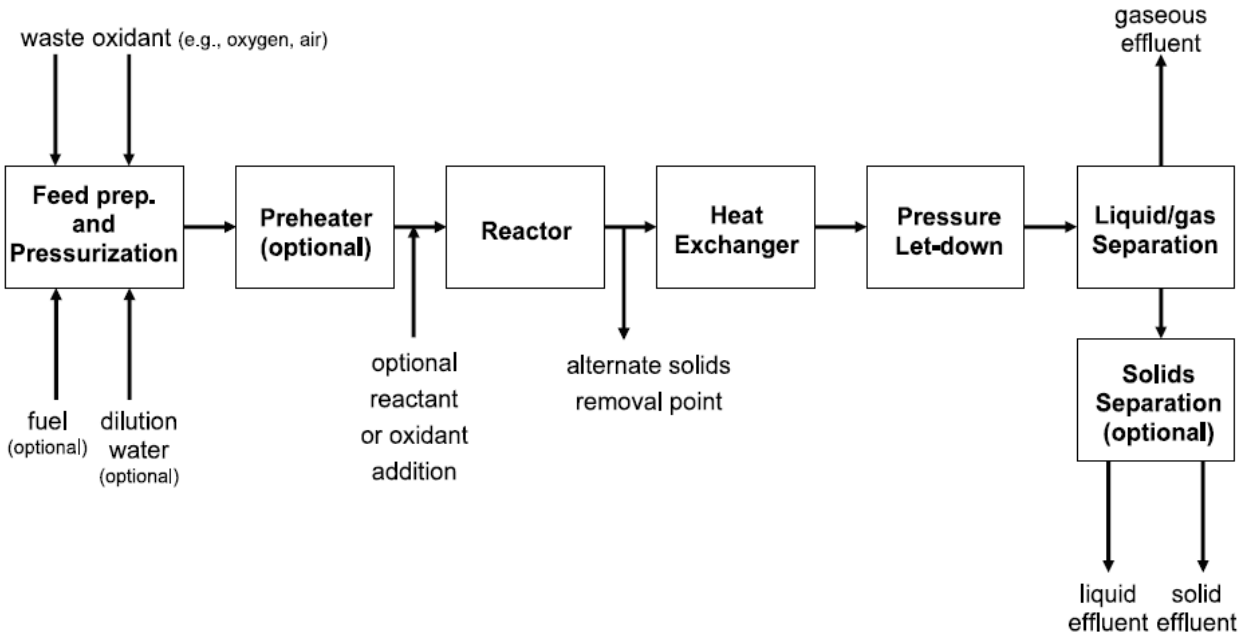


Figure 4: Basic SCWO process (Marrone et al., 2004).

Feed Preparation and Pressurization

In this section aqueous organic of 1-20wt% and oxidant solutions are prepared and delivered into the SCWO system, then followed by pressurizing and preheating to reach desired reaction conditions (above 374^{o}C and 22.1 MPa) and to allow for oxygen formation from hydrogen peroxide decomposition. On large scales, using secondary fuels (alcohols) is another option to minimize the heat needed to reach reaction temperatures (Cocero et al., 2000a).

Reaction

Delivered organic and oxidant solutions are mixed at the inlet of reactor under SC conditions where then exothermic oxidation reaction starts simultaneously when both reactants are contacted at a temperature of 400-450^{o}C and a pressure of 25 MPa. SCW medium provides complete miscibility between organics and oxidant that facilitates for a rapid reaction.

Cooling and Depressurization

After the oxidation reaction, the hot effluent stream (usually at > 400^{o}C and 25 MPa) is cooled down through the cooler and then depressurized to ambient conditions (25^{o}C, 1 bar), which allows liquid and gaseous phases to be formed and separated through a liquid - gas separator. In the case of complete oxidation, a typical reactor exist stream contains water, CO_2, N_2 and O_2. A heat exchanger is also the unit where heat can be recovered and integrated to the system on pilot and large scale units. For example, hot effluent from the reactor can be heat exchanged with the coming feed for preheating purpose (Bermejo et al., 2004, Kritzer and Dinjus, 2001). Also, the recovery of excess heat when exist can be used to generate steam either to produce electricity or hot water (Cabeza et al., 2011).

2.6.4 SCWO Operating Conditions

SCWO performance is influenced by temperature, pressure, initial concentrations of reactants (organic and oxidant) in addition to residence time. This section provides the role of various operating conditions and their ranges. The choice of operating conditions relies on the feed composition and the needed degree of removal.

Temperature and Pressure

Operating temperature is the most influential factor on SCWO conversion due to its role to enhance molecule collision. For example, reaction rate can be enhanced in which the yield is raised by a factor of 10 by increasing the temperature by 100 K (Brunner, 2009a). Others have reported that at higher temperatures above 650^{o}C, no intermediate compounds have been found in SCWO (Cocero, 2001). SCWO process usually operates at a temperature range of 400-650^{o}C and the temperature must be high enough in which free radical reactions proceed rapidly (Veriansyah and Kim, 2007). Also, increasing temperature minimizes the residence time needed for oxidation (Segond et al., 2002). It has been reported that the typical SCWO pressure can reach the range of 24-50 MPa (Kritzer and Dinjus, 2001). Supercritical pressure above 22.1 MPa has a negligible effect on the destruction efficiency, but its value could regulate salt appearance. For instance, Brunner (2009b) has reported that high pressure is necessary to enhance the solubility of inorganics and thus prevents salt formation due to increasing medium density. However, higher pressures are ideal for corrosion appearance.

Oxidant

There are common oxidants that are used in SCWO such as hydrogen peroxide, pure oxygen and air (Schmieder and Abeln, 1999). Oxidant selection is governed by the scale and process

economics. In lab-scale facilities, liquid hydrogen peroxide is preferred (easier to handle) to avoid oxygen compression challenge of gas compression, while with large-scale units using oxygen or air is preferred due to the high cost of hydrogen peroxide (Cocero, 2001, Martin et al., 2011). Also, it is more economical at industrial scale to use pure oxygen due to the high compression cost of air and also to avoid nitrogen (Bermejo and Cocero, 2006). Hydrogen peroxide in SCWO can be used as a primary oxidant in which it thermally decomposes in reaction zone directly into highly reactive species (hydroxyl radicals), or as a source of oxygen where it thermally decomposes into oxygen through pre-heater. Svishchev and Plugatyr (2006) has pointed out that in many lab-scale studies that H_2O_2 has higher efficiency than oxygen due to directly generated reactive hydroxyl radicals, while oxygen needs an initial step to attack organics in order to generate these species. Pinto (2004) also have reported that aqueous H_2O_2 is easier to be pumped into the system and has better mixing characteristics compared with oxygen gas. In SCWO process the oxidant can be varied from stoichiometric to excess amounts. Cocero et al. (2000b) has suggested that the optimal dosage of oxidant is 120% of the stoichiometric needed amount.

Residence Time

Residence time varies based on the used temperature and the range of corresponding flow rate at a constant reactor volume. Its range selection relies on the needed degree of destruction, the range of flow rates that the pumps can deliver and obtaining turbulent flow.

2.6.5 SCWO Process Design Considerations

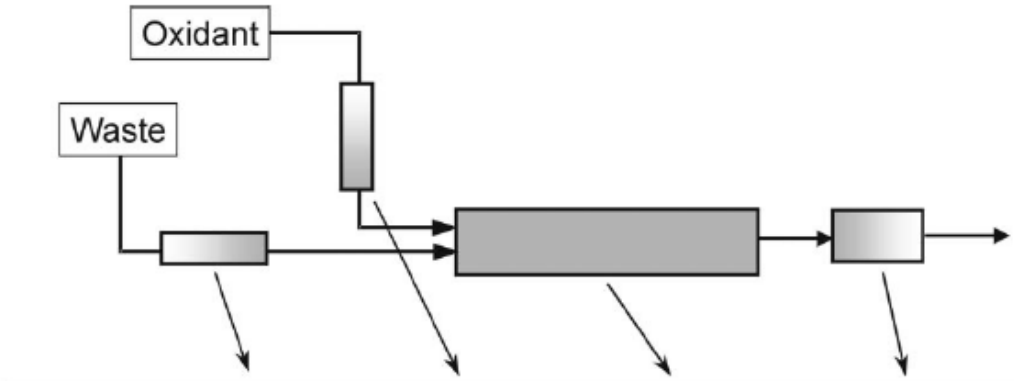
Certain considerations must be considered during the selection of proper process design in order to avoid any technical challenges that could affect its performance. Gloyna and Li (1998) have outlined the main design aspects for an efficient SCWO system. These include; influent pre-

treatment, construction materials, heat and system integration, monitoring, effluent manipulation and ash disposal. The target waste composition, concentration and needed degree of treatment are significant considerations for selecting the materials of construction, process design and energy assessment. If a complete removal is needed for organic waste, then residence time and reactor volume are the key design parameters. However, some SCWO processes aim to synthesize new chemicals or convert organic waste into beneficial by-products using hydrothermal conditions (as hydrolysis). Therefore, operating conditions, optimized process design and oxidant (for partial oxidation) would be the main design considerations. Also, location, availability of staff and raw materials are essential factors.

2.6.5.1 SCWO Engineering Challenges

Several reviews and research have outlined the common engineering challenges in SCWO and the developed novel designs, construction materials and specific operating techniques for SCWO systems (Gloyna and Li, 1998, Kruse and Schmieder, 1998, Kritzer and Dinjus, 2001, Cocero, 2001, Kritzer, 2004, Hodes et al., 2004, Marrone et al., 2004). Although some companies have commercialized SCWO at large scales, this technology still has its challenges, such as salt precipitation and corrosion (Veriansyah and Kim, 2007). These engineering challenges could affect SCWO process performance and reliability especially on large scales. Hetero-atom content (halogens, sulphur, phosphorous) decomposes into its corresponding mineral acids that cause corrosion under supercritical conditions. In general, the presence of oxidant and the change in density based on temperature-pressure variations are an ideal environment for aggressive species. Shaw et al. (1991) have reported that SCW is highly corrosive particularly if halogenated compounds are present, where using special alloys for SCWO reactor are needed. On the other hand, neutralizing the formed acids by alkalis (to control corrosion) generates salts that are

insoluble in supercritical medium, in which their precipitation is another challenge. Salts can also exist in waste stream or produced during treatment as inorganic species. Formation of salts eventually causes scaling that leads to plugging through the system and thus interruption of operation, in addition to heat transfer limitations between inner and outer reactor surfaces. Kritzer and Dinjus (2001) showed that these challenges can be avoided using innovative construction materials and reactor concepts. Figure 5 shows the SCWO process parts that could be affected by these challenges and causes. In general, severe corrosion and salt precipitation appear in the heat exchanger and in the reactor respectively.



	Waste Preheater	Oxidant Preheater	Reactor	Heat exchanger
T (°C)	25 → 380		600	600 → 25
Reactions	Pyrolysis may occur		Oxidation	Formed acids dissociate
Agressive species	Salts, (HCl) no O_2	O_2	HCl; O_2	H^+; Cl^-; O_2
Main Problem	Slight corrosion	No problem	Salt precipitation	Severe corrosion

Figure 5: Conventional SCWO process and reactions leading to problems in particular parts of the plant (Kritzer and Dinjus, 2001).

2.6.5.2 SCWO Reactor Configurations

Reactor designs and geometry play an essential role to overcome the common challenges in SCWO systems and thus improving durability. The performance of the reactor actively relies on its design and operating conditions. There are four essential reactor concepts that have been developed to overcome SCWO technical challenges, which are tank, tubular and transpiring wall and cooled wall reactor (Schmieder and Abeln, 1999, Cocero, 2001, Marrone et al., 2004, Bermejo and Cocero, 2006, Queiroz et al., 2015). Tank reactor was the first developed design in order to dissolve insoluble inorganics, where undissolved sticky salts at supercritical conditions accumulate at the bottom of the tank in order to be removed (Marrone et al., 2004). As shown in Figure 6, the tank reactor consists of two temperature zones both at supercritical pressure, the reaction zone in the upper part to keep the reactor above critical temperature and a cool zone in the lower part to dissolve the salt precipitant at subcritical temperature. In a vertical cylindrical vessel the pressurized feed and oxidant are injected downward by means of a co-axial nozzle into the hot zone located in the upper zone of the vessel, in which oxidation of the organics and oxidisable inorganic takes place, while gaseous effluents from this phase are discharged from the top region of the vessel. Insoluble salt that is initially present or formed in the supercritical fluid phase forms dense brine droplets or solid precipitates that fall by gravity into a liquid phase maintained in the bottom zone of the reactor by injection of cold water. The bottom lower temperature liquid phase provides a medium to re-dissolve soluble salts, and to form a slurry of insoluble materials. The resultant brine solution or slurry is removed from the pressure vessel via a discharge nozzle located in the lower zone of the vessel.

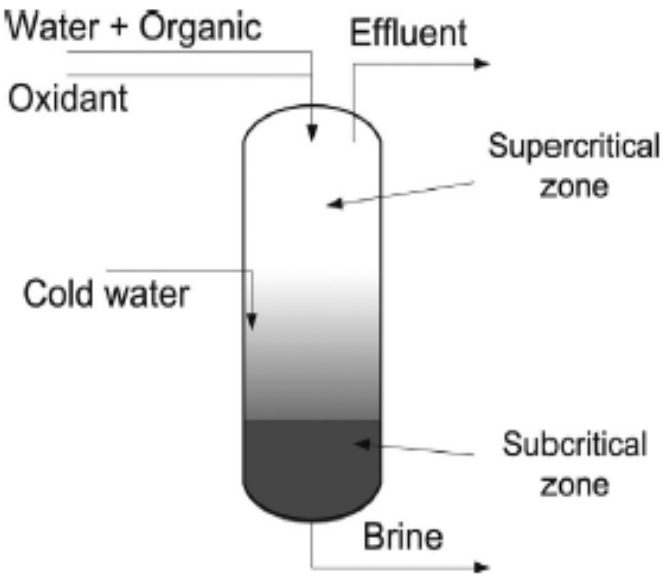


Figure 6: Schematic diagram of tank reactor (Marrone et al., 2004).

Transpiring wall reactor (TWR) is more recent reactor concept that was developed from basic tubular. The concept behind the TWR design includes a dual shell consisting of an outer pressure-resistant wall and an inner porous wall that surround reaction chamber. Through the porous wall, supercritical water will circulate to form a thin and cold water layer that protects reactor wall from salt deposition and in addition to corrosion (Shaw and Dahmen, 2000, Bermejo et al., 2005). Part of the reactor effluent can be used as cleaning fluid at the end of the salts elimination. The only disadvantage is that a high quantity of additional water is needed for TWR that could increase the cost (Bermejo and Cocero, 2006). The schematic diagram of TWR is shown in Figure 7.

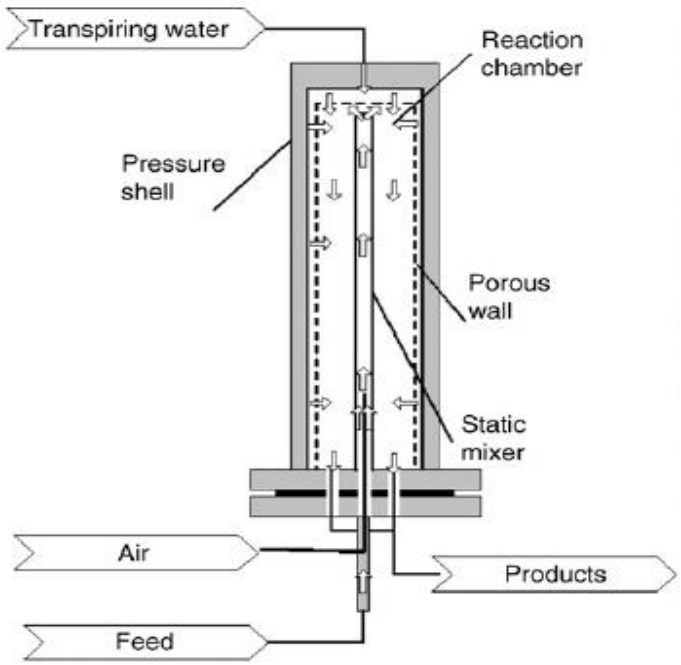


Figure 7: The schematic diagram of transpiring wall reactor (Bermejo and Cocero, 2006).

Tubular reactor is the simplest reactor that is widely used especially in small laboratory units to study the viability of SCWO and to determine kinetic parameters (Benjamin and Savage, 2004). Its suitability for obtaining kinetic data is due to the ability to maintain temperature profile along the reactor in addition to well mixing feature. Plug flow reactors achieve highest conversions in short residence times since the SCWO process kinetics is pseudo first order with respect to the waste concentration (Bermejo and Cocero, 2006). It is suitable for waste feeds with very low salt concentrations or generating salts and solids which are non-sticky, otherwise plugging will occur. Using a small diameter with high-circulation fluid helps to avoid salt deposition with feeds of low salt content (Cocero, 2001). It has more flexibility for the expansion to industrial to treat larger capacities. Nowadays, tubular reactors are used in different industrial uses such as the AquaCat® process (Johnson Matthey site in Brimsdown, UK) as shown in Figure 8.

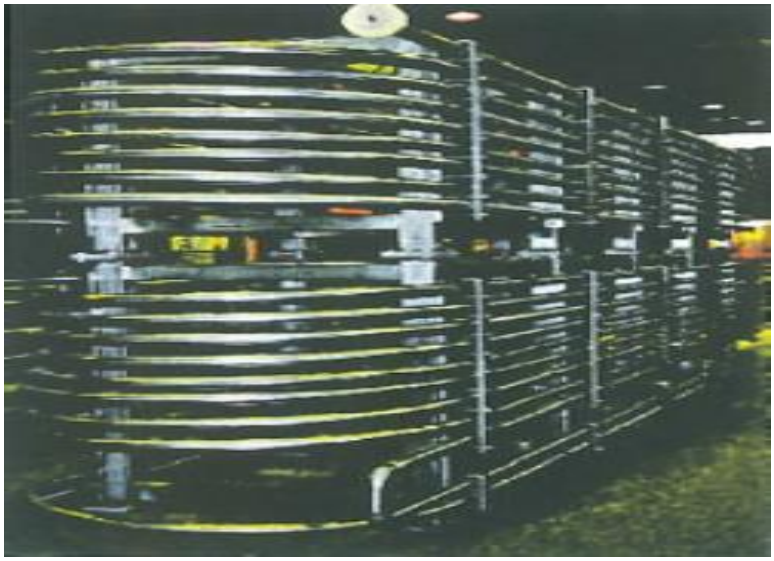


Figure 8: View of tubular reactor of the AquaCat® Process (Bermejo and Cocero, 2006).

Cooled-wall reactor is another design which cools the wall by coaxial introduction of large amounts of water. This type was developed at the Chemical Engineering Department of Valladolid University, Spain. In this type of reactor, temperature and pressure effects are isolated. This is achieved by using a cooled wall vessel, which is maintained near 400^{o}C, and a reaction chamber where the reactants are mixed and reaction takes place. This reaction chamber is made of a special material (e.g. ceramic) to withstand the oxidizing effect of the reactants at a maximum temperature of 800^{o}C and a pressure of 25 MPa. It is enclosed in the main vessel, which is pressurized with the feed-stream before entering the reaction chamber, so that it works at about 400^{o}C and does not suffer from the oxidizing atmosphere (Cocero, 2001, Bermejo and Cocero, 2006). This pressure vessel can therefore be made of stainless steel. Another additional advantage of this reactor design is that it is possible to preheat the feed inside the reactor that allows building a compact unit that is very appropriate for mobile units. Operation with this reactor is limited to low salt concentration wastes, to avoid plugging. Its diagram is shown in Figure 9.

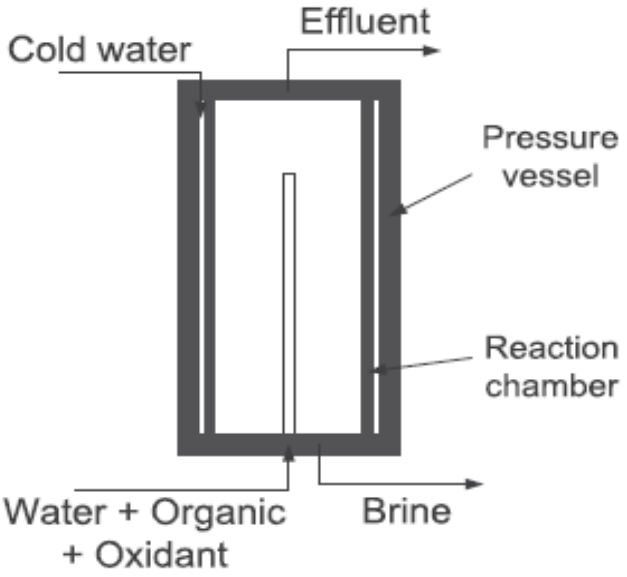


Figure 9: The schematic diagram of cooled wall reactor (Queiroz et al., 2015).

Moreover, there are some special designs such as centrifuge, reversible flow tubular, and concentric tube reactor that developed to mitigate salt deposition and corrosion (Cocero, 2001). Lastly, multi-oxidant tubular reactor is a special design that has been developed at the University of Birmingham to overcome the depletion of oxygen during the oxidation reaction (Kings, 2012), where this design was further investigated by other research group (García-Jarana et al., 2012, García-Jarana et al., 2013).

2.6.5.3 Materials of Construction

The selection of materials of construction under certain operating conditions is essential to resist corrosion. High variations of temperature and pressure, the presence of oxygen, extreme pH and the presence of aggressive species as chloride yield corrosion and affects SCWO system material (Gloyna and Li, 1998). Corrosion phenomenon, its mechanisms in SCW and the used construction materials have been intensively reviewed (Kritzer, 2004). Concisely, the most

common construction materials for SCWO components are; Stainless steels, nickel based alloys, titanium alloys and ceramic materials. Stainless steel (as SS 316) is a suitable choice to resist corrosion with non-heteroatom waste stream and at relatively low temperatures (300^{o}C-500^{o}C) otherwise severe corrosion will appear in the acidic environment. Table 2 shows the efficiency of nickel based alloys and titanium at different sub- and supercritical regions. It shows that corrosion can be mitigated by using specific materials for certain parts of the SCWO system, or selecting the suitable organic feed for the existing materials in addition to the range of operating temperatures and densities. In general, nickel and chromium based alloys such as Hastelloy C-276 and Inconel 625 have shown a good corrosion resistance in acidic environment especially with lower density in SC region. Shaw et al. (1991) has mentioned that recently liners from Titanium alloys have shown a good corrosion resistance (chloride attack) compared to Hastelloy C-276 and Inconel 625 alloys that do not provide enough protection. Others pointed out that titanium alloys have a high protection in strong oxidative conditions (Bermejo et al., 2005). Another review has reported that ceramic materials as SiO_2 and ZrO_2 could provide a better corrosion protection (Cocero, 2001).

Table 2: Corrosion resistance for titanium and nickel based alloys at different temperatures (Kritzer and Dinjus, 2001).

	$T < T_c$; high density		$T > T_c$; low density	
	Good resistance	Poor resistance	Good resistance	Poor resistance
Nickel-base	H_3PO_4, HF	HCl, HBr	All acids	$[H_3PO_4] > 0.1$ mol/kg
Alloys	Alkaline solutions	H_2SO_4, HNO_3		NaOH
Titanium	All acids	F^-	HCl	H_2SO_4, H_3PO_4

2.6.5.4 Salt and Scaling Management

Salt precipitation and the subsequent scaling (solids build up) is the challenge that can hinder the commercialisation of SCWO technology despite its efficiency to treat aqueous organic wastes. Hodes et al. pointed out that salts are formed (as solid phases) during the neutralization of acidic solution to control corrosion, or present in the feed stream or formed during reaction (Hodes et al., 2004). Oxides (solids) that have less adhesion also can be precipitated on internal surfaces. Due to the low solubility of inorganic salts in SCW, salts precipitate on internal surfaces and cause fouling that results in plugging, pressure build-up and heat transfer limitation. Therefore, apart from costly conventional cleaning methods, special reactor designs (previously explained) and/or practical operational approaches are needed to overcome the challenge of salt deposition.

Marrone's research team has reviewed the efficient commercial approaches that have been developed by several companies during the past two decades to control salt precipitation and solid build-up in SCWO system as shown in Table 3 (Marrone et al., 2004). Such approaches help to avoid system shutdown, safe time, labour and minimise the cost. In summary, these approaches consist of novel reactor designs and special management techniques. Also, some of these approaches can be applied to reduce corrosion effect such as in the case of the transpiring wall reactor design.

Table 3: Commercially developed approaches for SCWO salt/solid deposition management (Marrone et al., 2004).

Control method	Company holding patent (s) and/or using method	Function
Extreme pressure operation	Los Alamos National Lab, EWT	Avoids salt precipitation
Reverse flow, tank reactor with brine pool	MODAR	
Transpiring wall reactor	Foster Wheeler	
Adsorption/reaction on fluidized solid phase	SRI International	
Centrifuge reactor	MODEC	Allows for salt precipitation but prevents its accumulation on wall surface
High velocity flow	MODEC, Chematur, Organo	
Additives (provide surface for nucleation)	EWT, GA	
Low turbulence, homogeneous precipitation	HydroProcessing	
Crossflow filtration	University of Texas System, USA	
Density separation	HydroProcessing, GA	
Reversible flow, tubular reactor	Abitibi-Price	
Mechanical brushing	MODEC	
Rotating scraper	GA, MODAR	Removes salts after accumulation on surfaces
Reactor flushing	GA, Abitibi-Price, Chematur	
Additives (alter properties of salt mixture).	EWT, GA,	

Lastly, the physiochemical properties of SCW can be adjusted through the variation of temperature and pressure in the supercritical region (Bermejo and Cocero, 2006), and thus salt deposition and corrosion also can be controlled based on density variation. This indicates that in supercritical region, using higher density (via higher pressures or lower temperatures) would make salts more soluble and thus prevents precipitation and using lower density (via higher temperatures or lower pressures) would minimize the corrosion. Kritzer and Dinjus (2001) have pointed out that solution's density everywhere in the reactor must be below 200kg/m^3 in order to minimise corrosion.

2.7 Overview of SCWO Research Development

2.7.1 Fundamental SCWO Research

Earlier surveys of research focused on new SCW characteristics and its reactions (Savage, 1999). SCWO fundamentals, treatability and development were also reviewed by several authors (Holgate et al., 1992, Gloyna and Li, 1998). This included topics such as salt solubility, solids separation and product recovery. Others have investigated the role of SCWO, and the key engineering issues affecting SCWO development such as corrosion, salt scaling and process integration (Shanableh, 2000). They also discussed oxidation reaction pathways and kinetics for some models wastes. Reviews on SCWO efficiency to treat different wastewaters were also presented by other research groups (Cocero, 2001, Kritzer and Dinjus, 2001).

In general, this technology has shown its destruction efficiency, reliability and cost-effectiveness compared with other available conventional processes that allowed for its adaptation in several sectors to treat different classes of wastes either on research level or in industry as explained in subsequent sections.

Apart from hydrothermal oxidation effect there are other side SCWO reactions as hydrolysis (hydrothermal decomposition) that has been exploited to recover (synthesis) valuable chemicals from SCWO process and pyrolysis (thermal decomposition) that occurs in preheaters in the absence of oxidant.

2.7.2 SCWO of Nitrogenous Compounds

Nitrogen-containing hydrocarbons have obtained interest due to their abundance in a wide range of wastes, in addition to the difficulty to break down nitrogenous intermediates (due to their refractory nature). Nitrogen has a complex chemistry, in which it is important to understand the influence of nitrogen (hetero atom) on the physical properties and behaviour of SCW and its role in the reaction mechanisms in order to prevent undesired by-products. Nitrogenous organic compounds are available in several industrial effluents, e.g. chemical, petrochemical, pharmaceutical, food, petroleum and military industries. Moreover, municipal wastewater (domestic wastes and human metabolism), naturally produced proteins and amino acids are other effluents (Mishra et al., 1995). Also, they can be produced from sewage treatment and sludge in form of residues that contain large amounts of nitro-organics, urea and ammonia (Kiwi et al., 1994).

Several SCWO studies have been conducted on nitrogenous compounds ranging from simple, e.g. methylamine (Benjamin and Savage, 2004) to more complex, e.g. 2,4-dinitrophenol (Vera Pérez et al., 2004), pyridine (N.V.K. Aki and Abraham, 1999) and quinoline (Ogunsola, 2000). The majority of studies investigated the effects of different operation conditions on the destruction efficiency of SCWO process in forms of TOC, COD and nitrogenous compound conversions in addition to the determination of kinetics parameters. Some studies focus on the reaction mechanisms. Some of treated compounds are effectively oxidised in SCW, while others

are more refractory in this process unless severe conditions are used to achieve a high level of destruction. Besides molecular nitrogen, the oxidation of such compounds produces ammonia (NH_3), nitrite (NO_2^-) and nitrate (NO_3^-) that in certain concentrations need further treatment.

Ammonia has been widely investigated even it has a simple structure and has no carbon. Ammonia has obtained the interest as the most refractory (chemically stable) nitrogenous intermediate that is produced during the treatment of nitrogen-containing waste streams. It is a pollutant and toxic for aquatic life even in moderate concentrations and requires severe conditions to be removed, such as higher temperatures (>600^{o}C) and longer times (around 1 min) unless a catalyst is used.

Biological processes can be effectively applied to treat industrial wastewaters containing low concentrations of ammonia (20-80 mg/L). Above 90% of initial ammonia could be converted into nitrites in 7-14 days using *Nitrosomonas*. The nitrites in further treatment by *Nitrobactor* are oxidised to nitrates where complete oxidation of initial ammonia to molecular nitrogen was achieved in 7 days later (Fang et al., 1993). However, several industrial streams contain high concentrations of ammonia in which physical and chemical methods are used before the biological oxidation. Ammonia has obtained the interest by several research groups (Helling and Tester, 1988, Webley et al., 1991, Killilea et al., 1992, Goto et al., 1999, Cocero et al., 2000a, Segond et al., 2002, Ploeger et al., 2006b, Bermejo et al., 2008, Ding et al., 1998). It should be noted that some SCWO studies on ammonia showed some contradicting results that attributed to using different conditions, systems, feed composition and pH (Bermejo et al., 2008).

Helling and Tester (1988) pointed out that ammonia did not oxidise below 525^{o}C and a conversion of 5% was achieved at 540^{o}C in 6-13 seconds in a tubular reactor indicating its refractory nature. Also, they suggested higher temperatures (above 600^{o}C) and/or longer

residence times are needed for ammonia oxidation. Al-Duri's research team pointed that ammonia is the rate-determining step during the oxidation of nitrogenous compounds using a tubular system, in which studying its oxidation is essential to improve SCWO process design (Al-Duri et al., 2008). Others mentioned that ammonia in SCWO is the most refractory compound that needs higher temperatures above 600^{o}C to obtain a considerable removal at nearly longer residence time of ≤ 60 s (Ploeger et al., 2006b). For example, only 20% ammonia removal was obtained at 700^{o}C and a residence time of 2.5 s for 1 mM of ammonia using a tubular reactor. It has been reported that Ammonia oxidation was partially catalysed by the effect of reactor wall and its construction materials (Inconel 625) in which the oxidation rate in packed reactor was 4 times higher than that of tubular and with no nitrogen oxides observed in all runs (Webley et al., 1991). They also added that stoichiometric amount of oxygen did not limit the oxidation of ammonia as unreacted oxygen was always detected. Others found that ammonia removal increased with increasing temperature up to 41% at 690^{o}C and its conversion to N_2 was favoured thermodynamically over the conversion to N_2O at high temperatures (Killilea et al., 1992). Also, no NOx was detected and the levels of nitrite and nitrate were below 1 ppm. Applying higher temperatures above 600°C are adequate to remove the generated N_2O (Shaw et al., 1991). Goto's group pointed out that ammonia is the slowest reaction during full removal of organic wastes and thus its kinetic analysis is very essential for SCWO plant design. Their kinetic analysis showed that ammonia reaction was a first-order kinetics (Goto et al., 1999). They found a conversion of 30% at lower temperature 450^{o}C even after 4 hours of residence time using a batch reactor. Ding and co-workers studied the catalytic SCWO of ammonia in a continuous flow reactor and obtained a 96% ammonia conversion using MnO_2/CeO_2 at lower temperature of 450^{o}C and a residence time of 0.55 s and with no nitrite and only traces of nitrate and nitrous oxide, while without catalyst there was no conversion below 525^{o}C (Ding et al., 1998). They pointed that

more oxygen enhanced ammonia removal while increasing ammonia initial concentration has a negative effect. Cocero et al. (2000a) pointed out that the effect of different oxidant amounts was not the key parameter and an initial concentration of ammonia has no significant effect on ammonia conversion using a tubular reactor. They added that the concentrations of ammonia, nitrite and nitrate decreased with the temperature while more oxidant reduced ammonia but increased nitrite and nitrate. Therefore, the minimum levels of all nitrogen products were obtained with stoichiometric oxidant. Bermejo et al. (2008) observed in a packed bed reactor that the temperature needed for ammonia removal increases with its initial concentration, e.g. 710^{o}C for 1 wt% and 780^{o}C for 7wt% NH_3. Segond's team found that the conversion of ammonia to N_2 was enhanced considerably due to the catalytic effect of PFR wall (higher surface/volume ratio), in which a complete NH_3 removal can be achieved at conditions such as 600-630^{o}C, 24 MPa, 100% stoichiometric oxidant and 30 s when higher S/V ratio reactor was used (Segond et al., 2002). They showed that ammonia oxidised via both homogenous and heterogeneous (on the wall) mechanisms where the latter was pre-dominant. Also, they found that only 2-4% of ammonia removal was due to its hydrolysis in pre-heater. They pointed out that ammonia formation limits its large-scale usage unless catalyst, higher temperatures, or longer residence time applied. Others showed the efficiency of using nitrite and nitrate as oxidants on nitrogen speciation in a tubular reactor (Dell'Orco et al., 1997). Results showed that reacting MNO_3 (M is a monovalent cation; Li, Na, H) with ammonia significantly improved the conversion to N_2 and reduced the formation of N_2O and NO. Also, they added that higher temperatures and less oxidant dosage are preferred for nitrite and nitrate elimination. Shaw's study has reported that higher ammonia destruction can be achieved for waste feed with higher ratios of TOC/Tot-N (Shaw et al., 1991).

Several authors pointed out the influence of co-oxidation with other organics (co-oxidant fuels) on ammonia decomposition in addition to the feature of reducing operating temperature. This topic is thoroughly discussed in Section 2.7.6.

Benjamin and Savage examined the effect of water density and temperature during the SCWO of methylamine using a batch reactor and proposed the reaction pathways (Benjamin and Savage, 2004). They observed that methylamine conversion occurred through hydrolysis route. At lower water densities the pyrolysis was dominant, while hydrolysis became significant at higher densities (> 0.28 g/cm^3) and improved methylamine conversion. The same group also studied the reaction mechanisms and found the reaction proceeded through hydrogen abstraction (by $OH^{\bullet}$ radicals) at most temperatures studied, but below 400^oC it was initiated through oxygen addition to produce $CH_3NH_2O_2$ (Benjamin and Savage, 2005). The abstraction reaction was probably discontinued due to the generation of CO_2, CO, HCN and recalcitrant ammonia at lower temperatures.

Anikeev's work team investigated the SCWO of nitromethane, nitroethane and 1-nitropropane including the effect of water density on the conversion rate constant of these compounds in a tubular reactor (Anikeev et al., 2004, Anikeev et al., 2005). Results showed the rates were first-order kinetics that improved with the length of aliphatic chain.

Others studied the oxidation of 2-aminoethanol using a batch system under sub- and supercritical water conditions using H_2O_2 as oxidant (Funazukuri and Takahashi, 1999). They found an improvement in the TOC removal and in the yields of ammonia and CO_2 under supercritical conditions compared to subcritical. The TOC removal was enhanced by the presence of H_2O_2, while the oxidant did not affect the yield of ammonia.

Lee and Park (1996) and Lee et al. (1997) investigated the conversion of nitrobenzene and *p*-nitroaniline in SCW, respectively. Nitrobenzene decomposed even without oxidant and in the presence of oxygen its rate was faster where most of organic nitrogen converted to N_2 in a batch reactor. Similarly, *p*-nitroaniline using a tubular reactor remarkably decomposed without oxidant and when oxygen added its conversion significantly improved with a considerable reduction in NH_3. This was explained by the co-oxidation between ammonia and nitro-group (strong oxidant) from oxidised *p*-nitroaniline. They suggested that reacting nitro group-containing compounds with other nitrogen containing groups could decrease the formation of ammonia in SCWO.

Zhang and Hua also investigated nitrobenzene in a plug flow reactor and obtained above 95% conversion at 600^{o}C, 34 MPa after 160 s residence time (Zhang and Hua, 2003). They found above 60% of organic carbon was converted mainly to CO_2 and CO, and above 90% of organic nitrogen was decomposed to inorganic nitrogen species.

Chen et al. (2001) investigated the COD removals of some aromatic compounds such as aniline, nitrobenzene and phenol in SCW using tubular reactor. Their results showed that nitrobenzene was harder to be oxidised than aniline, while phenol was the easiest. Temperatures above 650^{o}C and 600^{o}C were needed for complete COD removals for nitrobenzene and aniline, respectively. Also, they showed that the COD removal of these compounds increased with temperature, pressure and residence times, even pressure effect was less than other variables.

Others treated high concentrations of 2,4-dinitrophenol (2,4-DNP) solutions using ammonium sulphate to evaluate the effects of temperature, oxygen excess and residence time on the removal of 2,4-DNP in addition to ammonia in a pilot scale tubular reactor (Vera Pérez et al., 2004). Results showed that 2,4-DNP was destroyed with TOC removal of 99.9%, while only around 37-50% of ammonia conversion was obtained. They showed that the large oxygen excess

was essential for a complete 2,4-DNP oxidation at 40 s, while CO and NO_x were negligible unless lower than stoichiometric oxygen was used. Phenol only appeared with less than stoichiometric oxidant. Further investigation for phenol showed that its TOC removal was less than that of 2,4-DNP where it seemed that 2,4-DNP decomposed to other refractory by-products other than phenol.

Qi et al. (2002) evaluated the effect of temperature, pressure, H_2O_2 dosage, residence time and aniline concentration using a lab-scale tubular reactor. Their results showed that these variables influenced the TOC conversion of aniline to higher or lower extent.

Gloyna and co-workers studied the destruction efficiency and/or kinetics of different model organic compounds, such as pyridine (Crain et al., 1993), acetamide (Lee and Gloyna, 1992), and dinitrotoluene (Li et al., 1993a). The latter study focused on the treatment of wastewater containing dinitrotoluene (DNT), 4,6-dinitro-ortho-cresol, phenol, 2,4-dinitrophenol, 2-nitrophenol and 4-nitrophenol using batch and tubular reactors with and without hydrogen peroxide. Their results showed that higher molecule weight components were destroyed rapidly, while lighter intermediates such as ammonia and acetic acid needed higher temperatures, longer residence times unless catalyst used.

Crain et al. (1993) oxidised pyridine in SCW using a tubular reactor and found that its oxidation improved with temperature. They identified pyridine intermediates and introduced a simplified reaction pathway for a first-order reaction with respect to pyridine.

Aki and Abraham (1999) also studied the oxidation of pyridine in a packed bed reactor and found that a conversion higher than 99% can be achieved in the presence of platinum catalyst (10 mg of Pt-doped gamma alumina) at temperatures as low as 370^{o}C.

Houser and co-workers studied the reactions of several nitrogenous compounds in SCW without oxidant to evaluate the ability of SCW to decompose such materials to less harmful ones and its ability to produce useful by-products. Decomposition rates of many nitrogenous aromatics such as benzylamine and benzylidenbenzylamine (Tsao et al., 1992), nitrotoluene, dinitrotoluene and phenylpyridine (Houser et al., 1996) and quinoline, isoquinoline and aniline all with and without $ZnCl_2$ catalyst (Houser et al., 1986, Li and Houser, 1992) were developed. For instance, authors found 70% of organic nitrogen during quinoline oxidation using a batch reactor was converted to ammonia. The kinetics of the catalysed reaction showed that it was first-order with respect to quinoline and the catalyst was found inversely proportional to water concentration. Also, hydrolysis reaction pathways were suggested for quinoline.

Tsao et al. (1992) examined in a batch reactor the SCWO of benzylamine (BA) and the hydrolysis of its intermediates as benzaldehyde, benzyl alcohol, benzoic acid and benzylidenebenzylamine (BBA) at 400^{o}C, 260 bar and a residence time of 15 minutes. They suggested the reaction pathways for BA oxidation/hydrolysis based on the break-up of C-N single bond in aromatic side-chain that forms a radical and alkylated aromatic or the hydrogen abstraction that forms a C-N double bond which can endure oxidation or decarboxylation. They added that the presence of biphenyl and benzene (confirms presence of phenyl radicals) and the presence of bibenzyl, benzyl toluene and toluene (confirms presence of benzyl radicals) implied that BBA formation was probably through benzyl radical pathway.

Fenuron was oxidised in a tubular reactor under sub- and supercritical conditions by Aymonier et al. (2000). It was initially decomposed to nitrobenzene, ammonia, nitrate and carbonaceous intermediates that further converted to CO_2, H_2O and N_2. The COD removal was 73.8% and 99.9% at 200^{o}C and 500^{o}C, respectively. They explained that ammonia decomposition

to N_2 at low temperature was due to the redox reaction between ammoniacal nitrogen and nitrogen oxidised forms (nitrate ions).

Ogunsola (2000) also studied the capacity of SCW to decompose heterocyclic quinoline and isoquinoline in a batch reactor. Results showed that both compounds were more reactive in hydrolysis than in pyrolysis and also both reacted diversely in SCW due to the different locations of N atom in each molecule. Intermediates such as hydroxyquinoline, toluene, methyl quinoline and aniline were identified during quinolone hydrolysis and the reaction pathways for both compounds were proposed.

Al-Duri et al. (2008) studied the oxidation of dimethylformamide (DMF) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) using a tubular reactor with H_2O_2 as oxidant. Removals enhanced with temperature where complete organic and above 90% TOC removal was achieved at 500^{o}C and 600^{o}C for DMF and DBU receptively. Also, conversions improved with oxidant dosage, residence time and initial organic concentration, while the effect of pressure in SC region was negligible. Ammonia remained in reaction effluent under these operating conditions where catalyst was suggested.

2.7.3 SCWO of Non-heteroatom Organic Compounds

Most of SCWO research has been conducted on the oxidation and hydrolysis of simple organic compounds (non-heteroatom) either aliphatic or aromatic. Several of these compounds are widely available in numerous industrial waste effluents, in which their investigation by SCWO is essential to assess their treatability by this technology.

The SCWO investigations included simpler organic compounds such as methane (Aki and Abraham, 1994, Savage et al., 1998, Sato et al., 2004), methanol (Cansell et al., 1998, Rice and

Steeper, 1998, Anitescu et al., 1999, Vogel et al., 2005, Fujii et al., 2011), ethanol (Schanzenbächer et al., 2002), formaldehyde (Osada et al., 2004), n-hexadecane and polyethylene (Watanabe et al., 2001) and benzene (DiNaro et al., 2000).

Savage et al. (1998) treated methane using a tubular reactor at 525-587^{o}C and 250 bar and found that CO was the highest yield product at low methane conversions, while CO_2 was the dominant at higher conversions of methane. Sato et al. (2004) examined the effect of water density on methane partial oxidation using a tubular reactor at 400^{o}C and O_2/CH_4 ratio of 0.03, where their results showed that product distribution shifted to partial oxidation products with increasing water density. It was obtained that the conversion of methane positively interacted with temperature, feed concentration, oxidant dosage and residence time.

The global reaction for methane can be to some extent shortened to the following route:

$$CH_4 \rightarrow CH_3^{\bullet} \rightarrow CH_2O \rightarrow HCO^{\bullet} \rightarrow CO \rightarrow HOCO^{\bullet} \rightarrow CO_2 \qquad (2.1)$$

Where the transformations are promoted through the reaction with radicals (mainly $OH^{\bullet}$) and O_2. Brock and Savage (1995) and Savage et al. (1998) showed further pathways between $CH_3^{\bullet}$ and CH_2O that includes species as $CH_3OO^{\bullet}$, CH_3OOH and CH_3O produced through the reaction with $HO_2^{\bullet}$ radical and O_2. A comparable mechanism was observed in the oxidation of methanol (Dagaut et al., 1996) in which methanol is converted to formaldehyde and ultimately to CO_2.

Brock and Savage (1995) showed that detailed kinetic modelling of C_1 compounds was predicted based on a mechanism that involved 22 species and 148 reversible free-radical reactions between these species, with a requirement that compounds should involve zero or one carbon atoms in addition to oxygen and hydrogen.

Rice and Steeper (1998) also conducted limited SCWO experiments on ethylene glycol and methyl ethyl ketone in a tubular reactor. The reaction kinetics was conducted on hydrogen (Holgate and Tester, 1991) and carbon monoxide (Helling and Tester, 1987, Watanabe et al., 2004) using tubular reactors to clarify the final intermediate reactions. Others modelled the reaction kinetics of simple fuels as H_2, CO and CH_4 by detailed chemical kinetic reaction mechanism (Dagaut et al., 1995).

Osada et al. (2004) oxidised formaldehyde in a batch reactor and achieved 90% conversion at 400^{o}C, 3-28 min reaction time and water density of 0.5 g/cm^3. The reaction proceeded further to produce intermediates such as CH_3OH and HCHO when the density was decreased to 0.17 g/cm^3.

Acetic acid also is another organic compound that was widely investigated (Lee et al., 1990, Meyer et al., 1995, Krajnc and Levec, 1997, Aymonier et al., 2001). Lee et al. (1990) studied the oxidation of acetic acid using hydrogen peroxide and oxygen as oxidants in a batch reactor. They examined temperatures such as 400, 450 and 500^{o}C, and different oxidant ratios of 1,2,3,4 and 5 times of stoichiometric needed at 450^{o}C. Also, they examined two specific densities as 0.15 and 0.35 g/ml at 5-30 min reaction times and a pressure range of 30-46 MPa. Results showed an increase in acetic acid conversion with temperature and residence time, and with fast conversion at early stages of the reaction. H_2O_2 was found to be more efficient than oxygen due to generation of $OH^{\bullet}$ radicals via H_2O_2 thermal decomposition. For instance, H_2O_2 was 8 times more efficient than O_2 at a density of 0.15 g/ml, 400^{o}C, and 5 min residence time. Considerable acetic acid removal of 97.5% was obtained with H_2O_2 at 500^{o}C, 10 min and 0.15 g/ml. At the same conditions, with O_2 only a conversion of 64.3% was achieved after 30 minutes. Also, the oxidant ratio of H_2O_2 was effective up to 300% oxidant. They pointed out that the effect of changing the density was negligible on the conversion compared to other effects. Aymonier et al. (2001) studied acetic acid in an adiabatic tubular reactor at an initial temperature of 400^{o}C, 250 bar and

residence time of 43.2 s, 26.4 s and 24.6 s. Residence time was changing with oxidant flowrate, while the flow rate of organic was constant (in which initial concentration of acetic acid was 3.35%, 3.92% and 4.9%, respectively). Results showed conversions of 30.5%, 98.4% and 96.9%, respectively. Higher acetic concentrations resulted in higher temperatures of 438^{o}C, 558^{o}C, 568^{o}C respectively above the initial temperature via the exothermic reaction that eventually caused much higher conversions.

Phenol and substituted phenols have obtained most of the interest. The determination of global kinetic parameters of phenol and the effects of operating variables such as temperature, pressure, reactant initial concentrations and residence time have been investigated by many research groups (Thornton and Savage, 1990, Gopalan and Savage, 1995, Krajnc and Levec, 1996, Minok et al., 1997, Rice and Steeper, 1998, Oshima et al., 1998, Martino and Savage, 1999, Matsumura et al., 2000, Portela et al., 2001, Chen et al., 2001, Lee et al., 2002, Vera Pérez et al., 2004, Fourcault et al., 2009). Some works have also been undertaken at subcritical conditions.

Phenol is one of the simplest aromatic compounds with a hydroxyl functional group (OH) that has obtained the interest due to its abundance in industrial waste effluents (Thornton and Savage, 1990). Therefore, oxidation and kinetics of phenol allow for using phenol as a model compound for industrial waste effluents and for intermediates produced during the oxidation of more complicated compounds.

Similarities were observed among the SCWO studies of different aromatic compounds. For instance, carbon dioxide (CO_2) is the product with the highest yield, even at low conversions of the aromatic component and at short reaction times. This indicates that once the aromatic ring is ruptured, the oxidation advances rapidly towards CO_2 formation (Holgate et al., 1992). Also, CO_2

was dominant even at low temperatures (that reduce CO oxidation to CO_2) which indicates other possible pathways for CO_2 generation. Another likeness is the formation of ring opening compounds as benzenediols and benzoquinones. The oxidation of aromatic compounds appears to proceed through parallel simultaneous reactions, such as forming dimers and ring opening compounds. The latter reaction seems to be favoured at higher temperatures and higher dosage of oxidant. Krajnc and Levec (1996) studied the SCWO of phenol at a temperature range of 380-450^{o}C, 230-265 bar using a tubular reactor and found that the stoichiometric oxidant was not sufficient for a complete phenol oxidation. Martino and Savage (1997) found that the substituted phenols have more reactivity than phenol when studied in a tubular reactor and that phenol reacts through two parallel routes such as the formation of phenol dimers and ring opening compounds, where dimers are further decomposed to ring opening products and ultimately to CO_2.

Thornton's study showed different phenol conversions ranged from 0-20% at subcritical pressure, small phenol initial concentration, or when a large oxygen deficit was used (such as 15% of stoichiometric oxidant) using a tubular reactor. The conversion reached 100% at high residence times, high oxidant ratios, and/or high temperatures. The phenol conversion was positively correlated with temperature, pressure, oxidant ratio and residence time. Also, the effects of temperature, oxidant ration and residence time were observed in Perez et al.'s work. They found that the reactant feed concentration had a small effect on phenol conversion, while the reactor pressure was not searched.

Thornton's work showed several organic intermediates that were formed during phenol oxidation with some that were larger than phenol molecule. They ranged from bi-substituted phenols (where another hydroxyl group substituted into the benzene ring, such as catechol, resorcinol, hydroquinone), to m-phenoxyphenols, dibenzofuran and 2,2-biphenol. Diversity of hydroxyl-substituted species is in agreement with a mechanism predicted on hydroxyl radical.

Other intermediates involved different carboxylic acids, such as formic acid, succinic acid and maleic acid in addition to p-benzoquinone and CO.

The phenol concentration was steadily decreasing while the concentrations of other intermediates increased to reach the maximum and then declined, that indicates the occurrence of parallel series of reactions. Minok et al. (1997) affirmed that the oxidation of phenol is probably initiated and promoted through parallel reactions in which oxygen radical ($O^{\bullet}$) reacts with phenol and water when oxygen used as oxidant. From the reaction of atomic oxygen radical with water, $OH^{\bullet}$ radicals are formed as follows:

$$H_2O + O^{\bullet} \rightarrow 2OH^{\bullet} \quad (2.2)$$

These generated $OH^{\bullet}$ radicals react with phenol in parallel with the reaction of $O^{\bullet}$ with phenol as follows:

$$Phenol + O^{\bullet} \rightarrow Intermediates \quad (2.3)$$

$$Phenol + OH^{\bullet} \rightarrow Intermediates \quad (2.4)$$

The rate constant of reaction 2.2 is smaller than those of reactions 2.3 and 2.4 by a factor of 10^2 (Minok et al., 1997).

Thornton's work shows that a diversity of potential complex intermediates should be formed after these two radical reactions. Thornton's work also detected iron, chromium and cobalt and thus concluded the presence of low levels of corrosion in their system that was made of Hastelloy C-276 for high temperature components and 316 stainless steel for other components. Iron and chromium are available in both alloys.

Minok et al. (1997) achieved phenol conversions from 11 to 99% corresponding mainly with residence times of 12-120 s. Also, the conversion of phenol was positively correlated with temperature and oxidant ratio. They found the reaction order with respect to phenol was unity, indicating the positive correlation between reaction rate and phenol initial concentration. The same study showed that the system pressure had no clear effect on the reaction rate when helium was used to pressurise the reactor. This observation is partly confirmed by Thornton's work that showed increasing the pressure increased final conversion of phenol, while the initial rate was kept constant. Oshima et al. (1998) found that the oxidation reaction of phenol was first order with respect to phenol and 0.48 with respect to the oxidant when investigated using a tubular reactor.

2.7.4 SCWO Hetero-Atom Compounds

SCWO is ideal for organic compounds that consist of carbon, hydrogen and oxygen where final products are CO_2 and H_2O. However, the presence of heteroatoms such as chlorine and sulphur can be more problematic that affects the process performance and applicability. Hetero-atoms during SCWO decompose to their corresponding acids (e.g. hydrochloric acid and sulphuric acid) that eventually cause corrosion, while neutralizing such acids by alkalis would form salts (e.g. chlorides and sulphates) and thus scaling. Heteroatom-containing organics (mainly as chlorinated) are widely available in several domestic and industrial waste effluents and have more risk to cause corrosion, and thus they have been examined by SCWO process to assess the ability of this technology to decompose such components. Also, the products from treating such components are not as benign as the products produced from other hydrocarbons, and thus it is necessary to assess to the need for further treatment for their product streams according to the treatment standards that shown in Section 2.1. Nitrogen atom has less potential

to form acid and thus corrosion but decomposes in SCWO into inorganic species as ammonia, nitrites and nitrates.

Several oxidation and/or hydrolysis studies were undertaken on thiodiglycol (Lachance et al., 1999, Veriansyah et al., 2007), methylene chloride (Marrone et al., 1998), chlorobenzene (Svishchev and Plugatyr, 2006), 2,4-dichlorophenol (Lee et al., 1990, Lin et al., 1998), 2,3-dichlorophenol (Kronholm et al., 2000), 2-chlorophenol (Li et al., 1993b, Lee et al., 2002), and catalysed by CuO/ZSM-48 (Lin and Wang, 1999), *o*-chlorophenol (Sun et al., 2007), 4-chloro-3-methylphenol (Kronholm et al., 2001), 1-chloro-3-phenolpropane, 2-chlorotolune, 4-chlorophenol (Houser and Liu, 1996), Aroclor (Anitescu and Tavlarides, 2000), polychlorinated biphenyl (PCB) such as 4-monochlorobiphenyl (Zhang, 1998) and 3-chlorobiphenyl (Hatakeda et al., 1999).

The oxidation of thiodiglycol (TDG-$C_4H_{10}O_2S$) in SCW was examined by Veriansyah et al., (2007). TDG was chosen since it is a refractory product during the hydrolysis of mustard gas and since it has the same C-S bond arrangement and similar density of mustard gas. Therefore, the similarity to mustard gas (chlorinated form of TDG) allows to that the treatment of TDG can be used as analogous to the treatment of this and similar chemical agents. They focused on the kinetics of sulphur heteroatom via the TOC removal since when TOC is removed; no organic sulphur would stay in the medium. They obtained TOC conversions above 90% after the SCWO of TDG in a tubular reactor at a temperature range of 397-617^{o}C, 25 MPa, oxidant excess of up to 4.4 times of stoichiometric demand and residence times of 9-40 s. For temperatures in excess of 600^{o}C, higher TOC conversion above 99.99% was achieved. It was shown via modelling the obtained data a TOC removal above 99.99% can be achieved in a residence time less than 30 s if more intense conditions such as temperatures above 600^{o}C and 150% of stoichiometric oxidant are used. The organic sulphur was converted to sulphuric acid (H_2SO_4 (aq)) and gaseous

hydrogen sulphide (H_2S), where sulphur balance showed that 95% of organic sulphur was converted to these components. The potential corrosion from the formed acidic components on the system hardware was not searched in this work. Lachance et al. (1999) showed that the TDG was completely decomposed in a tubular reactor to CO_2, H_2O, molecular sulphur and some sulphates at low temperatures as 400^oC and within seconds. Despite the generation of sulphates would suggest the formation of sulphuric acid, no engineering challenges were reported.

The SCWO of polychlorinated biphenyls (PCBs) was studied by Hatakeda et al., (1999). They oxidised 3-chlorobiphenyl (3-PCB), a mono-substituted biphenyl and Kanechlor KC-300, which contain from three to four chlorine atoms in each compound. Their oxidations were conducted under supercritical conditions in both batch and continuous reactors. Oxidants as H_2O_2 and pure O_2 were used in the batch system. At 400^oC, 300 bar and 5 minutes the obtained conversions of 3-PCB with H_2O_2 and O_2 were 95% and 20%, respectively. This suggested that the oxidation of 3-PCB proceeded through a free-radical mechanism that initiated by $OH^{\bullet}$ radicals produced via H_2O_2 thermal decomposition. At higher temperatures of 450^oC and 30 minutes, the conversions of 3-PCB increased to 99.999% and 40% with H_2O_2 and O_2, respectively. In the continuous reactor, at 400^oC, 300 bar and with using H_2O_2, above 99% of 3-PCB was converted during 10.7-101.7 s and above 99% of KC-300 was converted during 11.8-12.2 s. using 56% of stoichiometric oxidant showed that around 22 reaction intermediates were produced (probably decomposed) during this reaction, such as biphenyl, m-chlorobiphenyls, chlorinated dibenzofurans, dibenzofuran, other chlorinated aromatics and acetophenone. Chlorine in these components is transformed to $HCl_{(aq)}$. Accordingly, Hastelloy C-276 was used for reactor construction to reduce the risk of corrosion. Minimal traces of nickel, chromium, molybdenum, iron and cobalt were detected in liquid effluent that indicated the occurrence of some corrosion. Thornton and Savage (1990) observed much less corrosion when phenol was oxidised (has no

chlorine), in which this variation in corrosion levels is due to the presence of chlorine heteroatom in Hatakeda's work.

Sun et al. (2007) studied the dechlorination of *o*-chlorophenol (*o*-CP) in supercritical water using a tubular reactor. As already explained, the corrosive effect during the SCWO of chlorinated compounds can cause an engineering challenge. Therefore, Sun et al., (2007)'s work concentrated specifically on applying an introductory dechlorination step before the oxidation reaction. Their results showed that introducing potassium or sodium-based alkalis aided the dechlorination of *o*-CP via two pathways: hydrolysis, where ─Cl is replaced with OH producing catechol and resorcinol, and hydrodechlorination, where ─Cl is removed by a radical mechanism producing phenol as shown in figure 10. They observed that potassium alkalis helped dechlorination greater than sodium alkalis. Finally, they concluded that making a dechlorination step before the oxidation could help effectively minimise the corrosion.

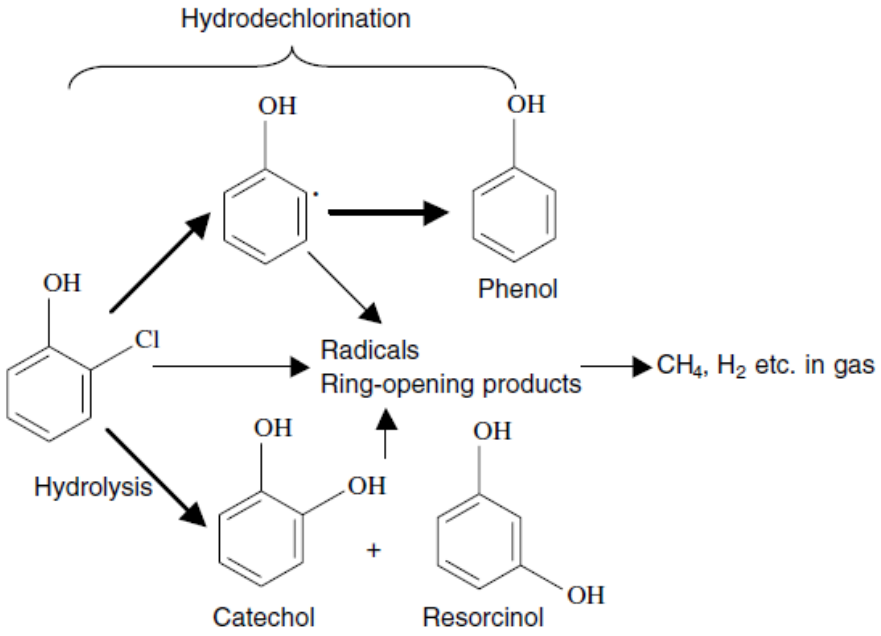


Figure 10: Dechlorination reaction pathways (Sun et al., 2007).

This study did not comment on the chloride salts, where it is known that salt precipitation could cause plugging issues and terminates the free-radical reaction. The chloride salts from the dechlorination step need to be removed through another step before introducing dechlorinated effluent to the oxidation reaction.

2.7.5 Co-oxidation in SCWO

Co-oxidation defines the system in which there are two or more organic components that are oxidised concurrently. Feed mixture that contain more than three species is considered a complex waste, where this will be explained in Section 2.7.7.

This section focuses more on the co-oxidation of the most refractory compound, i.e. ammonia, where the addition of other organic species as co-oxidants has been intensively investigated to assess the role of these co-oxidants on the destruction of ammonia. The interest of using co-oxidant fuels with ammonia was due to the fact that ammonia always requires higher temperatures, longer residence times and/or catalyst to be effectively destroyed.

In general, co-oxidant fuels have been reported to enhance the conversion of other associated organic compounds in SCW due to the following suggested reasons:

- Co-fuels oxidise faster (rapidly react) in the reactor when mixed with oxidants. Thus, this would accelerate the oxidation of other associated target compounds in SCW (Helling and Tester, 1988, Cocero et al., 2000a, Ploeger et al., 2007, Bermejo et al., 2008).
- Co-fuels enhance the generation of free-radicals during their conversions that enhance the conversion of treated compounds (Helling and Tester, 1988, Cocero et al., 2000a, Bermejo et al., 2008).

- High excess heat can be obtained during the oxidation of high-heating value compounds (e.g. co-fuels) that results in reaching higher reaction temperatures that enhances the conversion of treated compounds (via collision theory) and also this minimises the needed operating temperatures (Helling and Tester, 1988, Cocero et al., 2000a, Bermejo et al., 2008).

Cabeza et al. (2011) showed that increasing isopropyl alcohol (IPA) initial concentration from 1wt% to 5wt% resulted in increasing the temperature from 440^{o}C to 708^{o}C, respectively during IPA auto-thermal oxidation using a tubular reactor. Moreover, apart from improving the destruction, several studies have reported that the addition of high calorific value organics (e.g. alcohols as auxiliary fuels) can enhance the economic feasibility of SCWO process via the recovery and utilization of excess heat. This topic was discussed thoroughly in Section (2.8).

Several researchers showed the influence of adding other simple organic compounds (as alcohols) on the destruction of ammonia in SCWO (Helling and Tester, 1988, Webley et al., 1991, Killilea et al., 1992, Cocero et al., 2000a, Ploeger et al., 2007, Bermejo et al., 2008, Cabeza et al., 2011, Oe et al., 2007, Cabeza et al., 2014).

Webley et al. (1991) in a tubular reactor found that the usage of methanol (as a co-fuel) did not enhance ammonia conversion effectively at 530^{o}C, 245 bar and 6.7 s attributing this to using low concentrations for both reactants or due to the weakness of methanol. Oe et al. (2007) studied the role of methanol in the SCWO of ammonia using a tubular reactor at a temperature range of 560-620^{o}C, 25 MPa, residence time up to 1 min and air as oxidant. They found that using higher concentrations of MeOH increased the production of nitrous oxide (N_2O), nitrate and nitrite, and recommended catalyst usage to reduce N_2O at these conditions. Helling and Tester (1988) suggested that co-oxidants enhance free radical generation during co-fuel conversion, produce

extra heat and oxidise faster, which accelerates other organic compound decomposition as well as ammonia in SCW, though the acceleration mechanism itself is not fully understood. They reported that ethanol conversion using a tubular reactor increased from 16% at 484^{o}C to 99.5% at 541^{o}C. They found that the addition of ethanol did not affect significantly the removal of ammonia as only 5±5% conversion was obtained at 540^{o}C and suggested higher temperatures and/or longer residence times are needed. Killilea et al. (1992) studied the potential of ethanol (as auxiliary fuel) to decompose ammonia in a tubular reactor and found its presence improving ammonia removal at lower temperatures. For instance, a complete ammonia removal was obtained at 690^{o}C when ethanol used compared to only 41% for pure ammonia oxidation. In addition, minimum levels of nitrite and nitrate (<1ppm) were found and with no NO_x in the gaseous phase. Ploeger et al. (2007) found that the presence of ethanol enhanced ammonia decomposition using a tubular reactor from 20% (w/o ethanol) to 65% at a temperature of 700^{o}C, 246 bar, stoichiometric oxygen, 2.5 s and with 1 mM for every reactant. However, N_2O increased from 4-13% for pure ammonia to around 40% when ethanol used. Also, they observed that the removal of ammonia effectively enhanced with higher concentrations of ethanol. Lastly, they pointed out that ethanol has almost a similar effect to that of oxygen. Cocero et al. (2000a) found the presence of 2-propanol (as auxiliary fuel) enhanced the conversion of ammonia and also minimised the needed temperatures using a pilot plant tubular reactor. For example, they showed that optimum conditions for a complete ammonia destruction in the presence of 2-propanol were 600^{o}C, stoichiometric oxygen, 25 MPa and 43 s and with minimum concentrations of nitrite, nitrate, N_2O and NO_x. They explained that this was due to the previously mentioned reasons. In addition to ammonia, Cocero's work also examined the effect of IPA on the destruction of aniline, acetonitrile and pyridine and found the maximum conversions of TOC and N and the optimum conditions for these conversions were similar to those seen during ammonia oxidation,

which indicates that similar results can be obtained in SCWO using IPA as a co-fuel regardless of the molecule type or nitrogen bonds. Bermejo et al. (2008) investigated the role of IPA (as auxiliary fuel) on high concentrations of NH_3 (up to 7wt %) in auto-thermal continuous flow reactor. They found that complete ammonia decomposition can be achieved for 7wt% NH_3 at conditions of 780^{o}C, stoichiometric air and 40 s in the presence of IPA and with minimum levels of nitrate. Cabeza et al. (2011) used IPA as a co-fuel needed to form hydrothermal flame in a tubular reactor with refractory ammonia as IPA produces the needed combustion operation temperature. They found that increasing IPA amounts resulted in higher temperature and thus better removal in a very short reaction time. For instance, they obtained a total N removal of 94% and TOC removal above 99% for ammonia mixture at a temperature of 710^{o}C and only 0.7 s residence times compared to similar removals at 800^{o}C and 1 min with flameless reactor. Furthermore, no NOx or dioxins were detected as in case of conventional combustion. Cabeza et al. (2014) studied the role of IPA on ammonia removal using a lab-scale tubular rector at 400-525^{o}C, 250 bar, and 2-10 s with H_2O_2 as oxidant. They found that ammonia removal enhanced to reach 35% with increasing IPA/ammonia ratios (from 0-0125), then decreased at higher ratios (as > 0.5). Nitrate increased at higher IPA/ammonia ratios, while nitrite was negligible. Temperature increased ammonia removal from 10% to 30% at 400^{o}C and 525^{o}C, respectively. Also, they pointed out that stoichiometric oxidant is optimum for better ammonia destruction and less nitrate and nitrite.

Co-oxidation of other organic compounds using co-fuels was also investigated on other refractory compounds such as acetic and methylphosphonic acids. Cabeza et al. (2011) found with the presence of IPA the TOC removal of acetic acid mixture could reach 99% at a temperature of 710^{o}C and 0.7 s in hydrothermal flame reactor compared to 90% at 400-600^{o}C and 4-30 s in the absence of IPA in a tubular reactor (Meyer et al., 1995). Ploeger et al. (2006a)

studied the co-oxidation of hetero-atom methylphosphonic acid (MPA) using ethanol in a plug flow reactor. They found that using higher concentrations of ethanol improved the destruction of MPA from 30% with 1mM ethanol to 40% with 2.4 mM ethanol when MPA was 1mM at a temperature of 473^{o}C, stoichiometric oxidant and residence time of 9 s, while in the absence of ethanol only 14% MPA conversion was obtained. They attributed this effect of ethanol to the same reasons mentioned previously in this section. However, some SCWO studies also showed some contradicting results with the co-oxidation of ammonia with co-fuels (Bermejo et al., 2008).

2.7.6 SCWO of Specific Wastes

Spent ion exchange resins are an example of the wastes that currently has no efficient treatment approach (Leybros et al., 2010). Ion exchange resins are commonly used in nuclear industry to remove radioactive waste and also to minimise corrosion (IAEA, 2002). Therefore, after treatment the resins are highly loaded with radioactive contaminants that require an efficient treatment. Currently, thermal treatment such as incineration is applied to decontaminate the radioactive resins. However, although the incineration can achieve an adequate treatment, off-gas that is highly loaded with SO_2, SO_3 and NO_x can be released in which an efficient off-gas treatment system is required. Also, radionuclides such as Caesium and Ruthenium are volatile at high temperatures (above 800^{o}C) that also complicates off-gas disposal. Leybros's paper studied the application of SCWO to treat contaminated resins using double shell stirred reactor. The achieved TOC removal of treated resins ranged from 95 to 98%. Also, the complex components such as polystyrenic species were converted into simpler compounds such as benzoic acid, acetic acid and phenol. However, nitrogenous heterocyclic compounds did not decompose, while sulphur in the feed was converted into sulphate ions. This work did not explain the presence of radionuclide contaminants and their fate in SCWO. However, the obtained already stated

promising results showed the efficiency of SCWO as a unit operation to treat resins and its ability to reduce the off-gas challenge associated with incineration.

2.7.7 SCWO of More Complex Wastes

In addition to the oxidation of single-component and co-oxidation of bi-and tri-component systems, the SCWO of multi-component (more than three) waste has also been conducted in lab- and pilot-scale. Treating such complex waste by SCWO is essential as it mimics the oxidation of real complex industrial wastewaters and thus enables to study the effectiveness of this process when applied to large-scale applications. As the determination of the removal of TOC, COD, organic compounds is important to assess the process destruction efficiency, also monitoring engineering challenges as corrosion and salt plugging is essential to evaluate the reliability.

The SCWO of dyehouse water was conducted at temperatures of 400-600^{o}C and residence times of 8-16 s using a lab-scale tubular reactor (Söğüt and Akgün, 2010). The treated wastewater was taken from a textile plant and included many complex dye compounds, such as dimethyl benzyl ammonium chloride (multi-ring aromatics) and acetic acid. The feed stocks consisted of relatively low concentrations of TOC (~860 ppm) and total nitrogen (~118 ppm). Also, it contained trace metals (such as iron, lead, chromium and calcium) and solids. They reported no corrosion or plugging, even though the presence of chloride and methyl-bisulphate ions in the feed stocks. They have reported that solid particles were captured by a filter upstream the PFR.

The TOC removal ranged from 92% to 100% and was positively interacted with the temperature. Also, a notable removal of up to 93.8% was obtained at a high temperature of 650^{o}C through thermal decomposition. These results with the absence of engineering issues indicate the efficiency of SCWO to treat dyehouse complex wastewaters.

The oxidation of semi-synthetic cutting fluids (Biocut® and Servol®) was carried out using a pilot-scale SCWO reactor (at the university of Cadiz, Spain) and H_2O_2 as an oxidant at a temperature range of 400-500°C, 25 MPa and oxidant excess (Sánchez-Oneto et al., 2007). These oils were initially include water, mineral or synthetic oils, surfactants and other additives, that are normally anticorrosion compounds. The concentration of these constituents was varied between both fluids. The initial composition of both oils was as shown in Table 4. These oils are diluted with deionised water when used in metalworking operations to from emulsion that consumes heat during cutting and eventually a complex oily aqueous waste is formed.

Table 4: Composition of cutting fluids (Sanchez-Oneto et al., 2007).

	Biocut®	Servol®
Elemental analysis (wt.% dry basis)		
C	70.10 ± 0.42	45.56 ± 3.99
H	16.54 ± 2,61	17.75 ± 0.57
N	0.26 ± 0.05	3.22 ± 0.18
S	0.36 ± 0.04	0.28 ± 0.01
Others (rest to 100%)	12.74	33.19
COD ($g\,O_2\,g^{-1}$ concentrated cutting fluid)	2.264 ± 0.041	3.105 ± 0.031

SCWO was investigated since current treatment methods such as evaporation and filtration are inefficient for such waste. In this work they investigated the treatment efficiency and oxidation reaction kinetics of cutting oils. Results have showed that the TOC conversion increased with temperature to reach 97% for Biocut® and 98% for Servol® at 34 s and 9.7 s respectively. Also, they showed that the TOC removal kinetics for both cutting oils obeyed a pseudo-first order model. Finally, they concluded that the SCWO is an efficient treatment method; however, its economic feasibility is influenced by the heating value of the feed and the ability of recovering released energy.

2.7.8 Basic Kinetics and Reaction mechanisms of Simple Organic Compounds

2.7.8.1 SCWO Reaction Mechanism

Full knowledge of reaction pathways and mechanisms is essential to develop kinetic models, while identifying the main SCWO pathways is sufficient for engineering design purposes. Also, reaction rate of organics could be influenced by type and amount of formed recalcitrant intermediates. For example, ammonia and acetic acid are the most refractory compounds in which their formation represents the reaction rate-limiting step. SCWO mechanism is also influenced by the used oxidant type. For example, as previously discussed (in operating conditions section) hydrogen peroxide, oxygen and air are the most common used oxidants. Other oxidants such as as nitrite-nitrate (DellOrco et al., 1995) and potassium persulphate (Kronholm et al., 2000) also have been effectively used.

In SCWO environment, free-radical reaction mechanism is predominant as in case of WAO. It has been pointed out that in mono-phase medium and when water density decreases as

temperature exceeds the critical point and in presence of oxidant this mechanism overcomes ionic mechanism (Brunner, 2009b). The generation of high reactive radical can be through the selective attack of oxygen (if main oxidant) to weakest C-H bond of reacting organic molecule or with water. Then, rapidly and unselectively radical attacks the reacting organic or any organic specie in the reaction medium that promotes the oxidation and yields other radicals as shown in the following mechanism.

First, in preheater hydrogen peroxide thermally decomposes to oxygen as in reaction (2.5).

$$H_2O_2 \xrightarrow{\text{Heat}} \frac{1}{2}O_2 + H_2O \qquad (2.5)$$

Then oxygen reacts with organics as in reaction (2.6) to form organic radical ($R^{\bullet}$), and this reaction occurs at high temperatures where oxygen reacts readily with organics.

$$RH + O_2 \rightarrow R^{\bullet} + OOH^{\bullet} \qquad (2.6)$$

The reactive organic radical ($R^{\bullet}$) reacts with oxygen to generate organic peroxy radical ($ROO^{\bullet}$) as below:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \qquad (2.7)$$

Then, organic peroxy radical removes hydrogen atom from organic as in reaction (2.8) to produce organic hydroperoxide (ROOH) and another $R^{\bullet}$.

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \qquad (2.8)$$

The organic hydroperoxides are relatively unstable, thus their decomposition forms less carbon atom intermediates till reaching finally CO_2.

2.7.8.2 SCWO Reaction Kinetics

Based on several studies for different organics, it has been found that a global rate law expression describes most of the SCWO reaction rates as shown below in equation (2.11). It has been found that the reaction order with respect to the organic is unity by using excess of oxidant. However, numerous studies showed that the oxidant has an order higher than zero as oxidant increases. Water has an order of zero as it is always in excess. It has been pointed out that high stability of small molecules produced during the SCWO reaction is responsible for the global kinetic process (Cocero, 2001).

$$\frac{-d[Organic]}{dt} = k[\text{Organic}]^a[\text{Oxidant}]^b[H_2O]^c = A\, e^{-E/(RT)}\,[\text{Organic}]^a\,[\text{Oxidant}]^b[H_2O]^c \qquad (2.11)$$

Where

k = reaction rate constant in $M^{1-a-b-c}\ s^{-1}$

A = pre-exponential factor in $M^{1-a-b-c}\ s^{-1}$

E = activation energy in J/mol

R = universal gas constant (8.314 J/mol.K)

T = reaction temperature in K

[Organic] = organic compound initial concentration (mol/L)

[Oxidant]= oxidant initial concentration (mol/L)

$[H_2O]$= water concentration (mol/L)

a = reaction order relative to organic compound

b= reaction order relative to oxidant

c= reaction order relative to water

Several SCWO kinetics studies have been conducted under controlled reaction conditions of temperature, pressure, residence time and reactant concentrations. Some of earlier kinetics studies targeted waste mixtures, such as military wastes, sludges and cutting oils, while later studies focused more on single-model compounds under carefully controlled conditions. Particular consideration has been given to determine global rate laws and reaction pathways. Several oxidation kinetics have been carried out by several research groups for different classes of organic compounds (all previously mentioned classes). Table 5 shows examples of selected SCWO kinetics work for several classes of organic compounds and waste mixtures.

Table 5: Examples of selected SCWO kinetic studies carried out by several research groups.

Compound	Reactor Type	Temperature (^{o}C)	Pressure (bar)	$[Organic]_o$ (mM)	Kinetic Parameters					Reference
					A (s^{-1})	*Ea* (kJ/mol)	*a*	*b*	*c*	
Ammonia	Tubular	640-700	246	1.9-7.0	3.16×10^{6}	157	1	0	0	Webley et al., 1991
Ammonia	Tubular	655-705	245	0.97	$10^{19.0\pm4.5}$	347±79.5	1	0.44	0	Ploeger et al., 2006.
Ammonia	Batch	450-550	300	--	3.16×10^{5}	139	1	0	0	Goto et al., 1999
Ammonia	Tubular	530-630	140-280	0.6-9.4	4×10^{8}	166	0.9	0.06	- 0.14	Segond et al., 2002
Ammonia	Tubular	410-470	276	8.6	$10^{14.1\pm1.6}$	189	0.63	0.71	0	Ding et al., 1998
Acrylonitrile	Tubular	300-552	250	0.27-2.1M	6.1×10^{3}	66.33	1.26	0	0	Shin et al., 2009
Hydrazine	Tubular	200-452	250	0.1 wt%	19×10^{3}	70.24	1	0	0	Plugatyr et al., 2011
Acetamide	Tubular	400-525	230-335	0.23-60.8	$10^{2.2}\pm10^{1.3}$	51±5.5	1	0	0.17±0.2	Lee and Gloyna, 1992
Methylamine	Batch	386-500	250	4-78	1.3×10^{6}	159	0.66±0.1	0	--	Benjamin et al., 2004
Nitromethane	Tubular	410	230-310	37	0.0055-0.017[$]	--	1	0	0	Anikeev et al., 2004/5
Nitroethane	Tubular	410	220-310	29	0.0052-0.0124[$]	--	1	0	0	Anikeev et al., 2004/5
1-Nitropropane	Tubular	410	230-320	22	0.0059-0.0142[$]	--	1	0	0	Anikeev et al., 2004/5
Pyridine	Tubular	426-525	276	1.4-5.2	1.3×10^{13}	209.5	1±0.3	0.2	--	Crain et al., 1993
Pyridine (on Pt/γ-Al_2O_3)	Packed bed	365-570	250	1000ppm[£]	$10^{31.45\pm3.9}$	299.2	1.82	0.42±0.1	--	Aki and Abraham, 1999
Quinoline	Tubular	480-650	50-300	0.1-0.4	2.7×10^{13}	226	1	0	0	Pinto et al, (2004)
p-Nitroaniline	Tubular	380-420	250	2.5-4.1 wt%	$1.3\pm3.4\times10^{9}$	128±35	0.85±0.1	0	-.91±0.7	Lee et al., 1997
Nitrobenzene	Batch	440-550	230	0.26-1.96	1.2±4.9	68±9	0.39±0.1	--	0.21±0.4	Lee and Park, 1996
Methanol	Tubular	442-571	276	0.12 M	1.67	85.9	1	0	--	Rice and Steeper, 1998
Methanol	Tubular	300-525	250	0.78 M	$10^{26.5}$	409	1	0	--	Cansell et al., 1998
Methanol	Tubular	400-500	253	45-83	$10^{18.6}$	254	1.6	0	--	Anitescu et al., 1999
Ethanol	Tubular	400-540	246	0.67-0.79	$10^{21.82\pm2.7}$	340	1	0	--	Helling and Tester 1988
Ethanol	Tubular	433-494	246	1	$10^{17.23\pm1.65}$	213.9±18	1.34±0.1	0.55±0.1	--	Schanzenbacher et al.,2002
H_2O_2	Tubular	450	50-340	--	$10^{13.4\pm1.2}$	180	1	0	0	Croiset et al., 1997
Hydrogen	Tubular	495-600	246	0.67-3.69	$10^{20.5\pm2.1}$	338±33	1	0	--	Holgate and Tester, 1991

Compound	Reactor Type	Temperature (^{O}C)	Pressure (bar)	[Organic]$_o$ (mM)	Kinetic Parameters					Reference
					A (s^{-1})	*Ea* (kJ/mol)	*a*	*b*	*c*	
CO	Tubular	400-540	246	0.75-3.9	$10^{7.25\pm0.53}$	120	1	0	0	Helling and Tester, 1988
Acetic acid	Tubular	475-600	246	1-2	7.9×10^{9}	168	1	--	--	Meyer et al., 1995
Acetic acid	Tubular	420-470	240	0.437-0.174	$4.4\pm0.8\times10^{11}$	182±13	1	0.3	--	Krajnc et al., 1997
Phenol	Tubular	300-500	250	50-593 ppm	$10^{1.34\pm0.77}$	39±10.7	1	0	--	Portela et al., 2001
Phenol	Tubular	507-585	276	0.32 wt%	1.86	108	1	0	--	Rice and Steeper, 1998
phenol	Tubular	380-440	190-270	828 ppm	89×10^{3}	99.6	1	0	--	Koo et al., 1997
Phenol	Tubular	380-480	250	0.03-0.39	$10^{2.34}$	12.4	0.8	0.5	0.42	Gopalan and Savage,1995
Phenol	Tubular	400-420	280	0.53-3.51	3.03×10^{2}	51.8	1	0.5	0.7	Thornton and Savage,1992
Benzene	Tubular	479-587	246	0.6	2.7×10^{5}	204	0.4±0.07	0.17	1.4±0.1	DiNaro et al.,2000
o-cresol	Tubular	350-500	250	0.022-0.588	$10^{7.1\pm2.4}$	33.7±9.6	0.54±0.1	0.35±0.2	1.46±0.7	Martino and Savage,1999
Trichloroethane	Tubular	409-474	276	0.5 wt%	2.98	286	1	0	--	Rice and Steeper, 1998
Tetrachloroethylene	Batch	400	240	--	0.167	18	1	0	--	Liang et al., 2002
2-Chlorophenol	Tubular	300-420	190-290	0.08-2.15	$10^{2\pm1.2}$	46	0.88	0.41±0.1	0.34±0.1	Li et al., 1993
2.4-Dichlorophenol	Batch	400-550	238	--	79.9	56.9	0.97	0	0	Lin et al., 1998
Aroclor 1248	Tubular	450-550	253	0.0575	$10^{17\pm0.1}$	186±2	2.09	0	-	Anitescu et al., 2000
4-Monochlorobiphenyl	Tubular	380-550	250	0.33-6.3	$10^{8.6\pm2.7}$	31.1±8.6	1	0	--	Zhang, 1998
Thiodiglycol	Tubular	397-617	250	1.8-21	1.6×10^{2}	41.53	1	0	--	Veriansyah et al., 2005
Food Wastes	Batch	400-450	240	28784 ppm[£]	41	37.3	1	0	--	Jin et al., 2001
Cutting oil wastes	Tubular	330-500	250	750 ppm	6.09×10^{2}	0.0455	1	0	--	Portela et al., 2001
Sewage Sludge	Batch	400-500	300	9724 ppm[£]	1.08×10^{4}	76.3	1	0	--	Goto et al., 1999
Alcohol Distillery Wastewater	Batch	400-500	300	22400 ppm[£]	7.85×10^{2}	64.7	1	0	--	Goto et al., 1999
Wastewater (on γ-Al2O3)	Tubular	418-513	220-300	3.99-28.1 COD	2.67×10^{2}	55.45	0.81	0.49	--	Park et al., 2003

Compound	Reactor Type	Temperature (◦C)	Pressure (bar)	[Organic]$_o$ (mM)	Kinetic Parameters					Reference
					A (s^{-1})	*Ea* (kJ/mol)	*a*	*b*	*c*	
Winery Wastewater	Tubular	300-500	250	9200 ppm£	8.6×10^4	81.06	1	0	--	Portela et al., 2000
Olive Oil Mill Wastewater	Tubular	380-500	250	1200 ppm	15-30	35	1	0	--	Rivas et al., 2001

Notes:

[Organic]$_o$: organic initial concentration at reactor conditions in units of mM unless stated.

a,b,c: represent order of reaction with respect to organic reactant, oxidant and water.

$: specific reaction rate constants.

£: initial concentration of organic reactant at ambient conditions.

2.8 SCWO Energy and Economics

Apart from the destruction efficiency, several authors have highlighted the potential of recovering and integrating excess heat from SCWO system especially on large scales that makes this process economically feasible (Cocero et al., 2000a, Kritzer and Dinjus, 2001, Cocero et al., 2002, Griffith and Raymond, 2002, Bermejo et al., 2004, Bermejo et al., 2008, Sánchez-Oneto et al., 2007, Cabeza et al., 2011). Oxidation reactions of SCWO are exothermic especially with feeds of high calorific value where the system can be auto-thermally operated. Simply, after start-up and when auto-thermal state is reached the external energy source can be switched off where the recovered heat via heat exchanger is used to pre-heat the feed. Commonly, the recovered energy is used to pre-heat reactant feed and to maintain reaction temperatures which results in process integration on scale up (Cocero et al., 2002). It has been practically shown on a pilot plant that excess heat from hot effluent stream is employed to pre-heat the waste stream or any other feed through heat exchangers (Kritzer and Dinjus, 2001, Bermejo et al., 2004). Also, this heat can be utilised to produce hot water for other applications or to produce steam for electricity production. Some conducted an energy analysis for the SCWO of disposed wastes and have found that the hot effluent stream from specific feeds (high calorific feed) can produce an amount of energy sufficient to preheat the feed from ambient temperature to 400^{o}C in addition to generating an electric energy comparable to that consumed by air compression and high-pressure pump (Cocero et al., 2002). Others reported that apart from organic waste, recovering the released heat from using high calorific value secondary alcohols (as auxiliary fuels) that used to improve oxidation reactions can improve the SCWO process energy efficiency as its usage for pre-heating the feed enable to reach energetically self-sufficient process (Cocero et al., 2000a). Also, the presence of such fuels would reduce the system operating temperature that usually

provided by an external heat source, which ultimately reduces the cost of this process. For instance, Bermejo's team operated auto-thermal reactor without external energy source by recovering excess heat from ammonia and isopropyl alcohol (IPA) oxidation (Bermejo et al., 2008). Others concluded that SCWO is an efficient destruction method. However, its economic feasibility is influenced by the heating value of the feed and the ability to recover the process released energy (Cabeza et al., 2011, Sanchez-Oneto et al., 2007). For instance, a diluted aqueous feed waste doesn't generate effluent with temperatures high enough that allows preheating the influent to the needed temperature. Therefore, the influent must be preheated through external heat source which weakens the energy efficiency of the entire process. Queiroz and co-workers showed that feed with high enthalpy value of 930 kJ/kg can provide excess heat that's enough to preheat the feed (energetically self-sufficient operation) to 400^{o}C when recovered or even to produce electricity (Queiroz et al., 2015). Also, wastes with a high heating value of 3800 kJ/kg, the feed can be introduced into the reactor without external heat source for pre-heating stage (Cocero, 2001). Generally, the given energy to the low heating value feed can be recovered and thus enhances process economics. In comparison with conventional methods, Eco Waste Technology (EWT) concludes that the cost for SCWO is only one third of the incineration cost in the US (Schmieder and Abeln, 1999).

2.9 Current status of Commercial/Industrial SCWO Technology

Several reviews have summarised the status of commercial SCWO facilities including pilot-scale units that used to support larger applications (Bermejo and Cocero, 2006, Marrone, 2013). They have reported that the SCWO is a viable technology for aqueous waste destruction despite the technical and operational challenges that have interrupted some of its applications since the first attempt by MODAR in 1980 to commercialise this process. Bermejo and Cocero (2006)

mentioned that some SCWO facilities have been stopped due to corrosion, plugging and the relatively severe operating conditions, in which further research is required to control these challenges. Table 6 shows details of several companies involved in commercialising SCWO technology along with constructed facilities (active & inactive), in which each company has its own specific designs and operating approaches to overcome the associated issues.

Organo Corp. of Japan built in 1998 a 63 kg/h full-scale SCWO facility based on MODAR process for Nittetsu Semiconductor for the destruction of semiconductor manufacturing wastes. Salt precipitation was the main challenges in the used MODAR vessel system. Organo and others licensees operated MODEC process in Germany with a 2000 L/day for a few years until 1996 to treat pharmaceutical wastes, bulb and paper mill waste, and sewage sludge.

GA and Foster Wheeler have been involved in several projects to treat various hazardous wastes for different US military forces. GA provided a full-scale SCWO system with a 949 kg/h for the US Army in 1999 to destroy hydrolysed VX nerve agent at the Newport Chemical Depot in Indiana. A Platinum-lined reactor and regular flushing were used to control corrosion and salt. Also, GA successfully treated chemical agents (HD, GB and VX) and munitions using smaller systems (pilot scale) during 2000 and 2001 for the US Army in support of a full-scale system. The same company operated a compact SCWO system in 1999 for the US Navy to process 45 kg/h of shipboard wastes that contained lube oil, halogenated solvents, hydraulic fluid, antifreeze and paints. GA also tested rocket propellants for the US Air Force using a 3.8 L/min pilot-scale unit in 1995. Previous smaller-scale tests were performed in titanium or Hastelloy-lined reactors for corrosion control with additives or regular flushing for salt mitigation.

Foster Wheeler operated a full-scale SCWO system for the US Army in Arkansas to treat a 36 kg/h of smoke and dye munitions. The same company also performed pilot-scale testing for both

US Navy and Army. In 1999, shipboard wastes were tested for the Navy at 36-95 kg/h, and the same system was used in 2000 to treat chemical agents (HD, GB and VX) and munitions for the US Army with negligible corrosion and salt challenges. Based on the testing results, the US DOD identified the SCWO as a favoured approach to destroy chemical weapons.

EcoWaste Technologies (EWT) operated in 1994 its first operating commercial SCWO facility for the Huntsman Corp. in Austin, TX to treat organic wastes consisted of alcohols, glycols and amines with a capacity of 1100 kg/h.

Chematur Engineering AB operated its first full-scale SCWO unit (AquaCat®) in 2002 for Johnson Matthey in the UK that used to recover platinum from spent catalysts while organic contaminants are destroyed. This unit was the largest SCWO facility in Europe and the world. The same company has licensed to Shinko Pantec Co of Japan to construct and operate a1100 kg/h SCWO facility for the treatment of municipal sludge.

Hydro Processing, LLC operated in 2001 a full-scale system for Harlingen Wastewater Treatment Plant in Texas that consisted of two Hydro Soilds® units, each with a capacity of 47 L/min of sludge feed. The system was to process both municipal and industrial wastewater sludge. Hydro Processing pointed that the operating cost of this process is $ 180/ton, compared to $ 275/ton for sludge disposal by land fill or land application.

SRI international granted the license to Mitsubishi Heavy Industries (MHI) that operated in 2005 its first full-scale AHO process in Japan for treating PCB wastes with a capacity of 6 tons PCB/day. Since 1998, MHI has carried out tests with PCBs in a pilot-scale facility achieving higher than 99.99% destruction.

Hanwha Chemical built in 2000 a full-scale SCWO facility in Korea for treating DNT/MNT and Melamine wastewaters. Also, it has been operating another full-scale SCWO plant for toluene diisocyanate treatment in Korea since 2008 (Marrone, 2013).

Innoveox operated in 2011 a full-scale SCWO plant for industrial waste in France. SCFI also operated its first commercial plant in 2012 in Ireland for wastewater treatment. Lastly, SuperWater Solutions operated since 2013 a full-scale facility for treating wastewater sludge in Florida. These three are the most recent companies interested in SCWO commercialisation.

Despite that some SCWO plants are no longer in operation due to previous mentioned challenges; by 2015 there are six active companies that globally have been operating five active full-scale SCWO plants in addition to seven plants in the planning stages. Most of these companies have also smaller SCWO units for research & demonstration. Moreover, there are several active pilot-scale systems for research at the universities of Cadiz, Valladolid and British Columbia in which all these efforts will support the commercialisation of SCWO technology.

Table 6: Full-scale commercial SCWO facilities currently in existence (Marrone, 2013).

Company	Licensees	Full-scale plants	Application
MODAR, Inc. (1980-1996)	Organo	Nittetsu Semiconductor, Japan (1998-2002)	Semiconductor manufacture wastes
		moved to university of Tokyo (2002-2010)	University waste (since 2002)
MODEC (1986-1995)	Organo, Hitachi, NGK	None (1991- 1996)	Pharmaceutical wastes, pulp and paper mill waste, sewage sludge
General Atomics (1990-present)	Komatsu, Kurita Water Industries	US Army Newport Chemical Depot, Newport, IN (1999-stopped)	Bulk VX nerve agent; other feeds treated in smaller-scale systems: chemical agents & explosives (US Army), shipboard wastes (US Navy), rocket propellant (US Air Force)
Foster-Wheeler (1993-2004)	Sandia National Laboratories	US Army Pine Bluff Arsenal, AR (1998-2002)	Smokes and dyes; other feeds treated in smaller-scale systems: chemical agents & explosives (US Army), shipboard wastes (US Navy)
EcoWaste Technologies (1990-1999)	Chematur	Huntsman Chemical, Austin, TX (1994-2000)	Oxygenated and nitrogen-containing hydrocarbons (e.g., alcohols, glycols, amines)
Chematur (1995-2007)	Shinko Pantec	Johnson Matthey, Brimsdown, UK (2002-2007)	Spent catalyst (recover platinum and destroy organic contaminants)
		Japan (2000-2004)	Municipal sludge
SRI International (1990-present)	Mitsubishi Heavy Industries	JESCO, Japan (2005-present)	PCBs, chlorinated wastes
Hydro-Processing	-	Harlingen Wastewater Treatment, Plant No. 2,	Mixed municipal and industrial

(1996-2003)		Harlingen, TX (2001-2002)	wastewater sludge
Hanwha Chemical (1994-present)	-	Namhae Chemical Corp., Korea (2000-2005)	DNT/MNT and Melamine plant wastewaters
		Fine Chemical Co., Korea (2008-present)	Toluene diisocyanate (TDI)
SuperWater Solutions (2006-present)	-	Orlando, FL (2013-Present)	Wastewater sludge
SuperCritical Fluids International (SCFI) (2007-present)	-	Eras Eco, Ireland (2012-present)	Wastewater treatment
Innoveox (2008-present)	-	Arthez-de-Bearn, France (2011-present)	Hazardous industrial waste

CHAPTER 3 - EQUIPMENT, MATERIALS, PROCEDURE, AND ANALYTICAL TECHNIQUES

This section illustrates the experimental segment of this research. This includes a full description of used equipment and how the system was run. Also, includes materials, procedures that used during all experiments and methods that were used for the analysis of all products of SCWO reactions and hydrothermal decomposition for DMF, DBU and ammonia.

3.1 SCWO Rig Description

Figure 11 shows the process diagram of the used lab-scale SCWO system in its final form after it was designed and built. This SCWO system consists of these main sections: feed delivery, reaction zone and effluent cooling, depressurizing and sample collection section. Reactions take place in plug flow reactor hosted in an electric oven.

3.1.1 Feed delivery

This section includes feed delivery to the system after pressurization. It consists of both organic and oxidant feed tanks that are linked to the rest of the system using two high-pressure liquid chromatography pumps (HPLC-pumps, PU-2086 plus, Jasco) and two-way valves in addition to the necessary tubes.

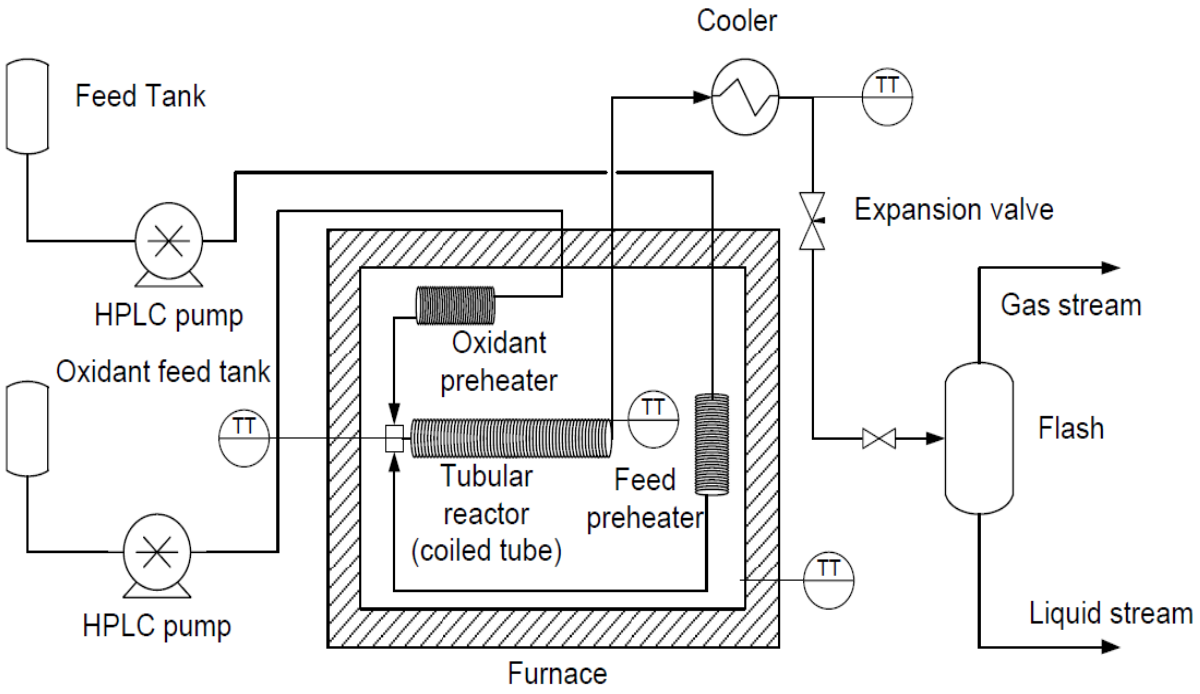


Figure 11: Laboratory scale SCWO apparatus and flow system.

The two-flow stream system is designed so that the organic solution and oxidant solution come into contact with each other only when they have been pressurized and preheated to the desired operating conditions. The aim of this is to let both streams reach the reaction temperature and pressure at the beginning of reactor and also to ensure that all H_2O_2 solution decomposes to O_2. Here, all feed tanks are connected to their HPLC pumps via 1/8in (O.D) Teflon tubing, while all tubing in the rest of the system are made of stainless steel (SS-316) with 1/16 in outer diameter (O.D) and 0.6 mm inner diameter.

Both organic and H_2O_2 solutions are delivered by two Jasco HPLC pumps (PU-2086 plus). Both pumps have a flow rate range from 0.001 to 20 ml/min and deliver precisely the desired flow rates during each experiment and with maximum operating pressure of 50 MPa. A constant pressure of 250 bars was used during all experiments. Pumps have less than 0.2 % (RSD) at 0.2 ~5 ml/min. Both pumps were calibrated while connected to the whole system at a mean operating temperature of 450^{o}C and pressure of 250 bar flowing distilled water. Calibration was done

before each set of experiments in order to know the real output flow rates and to perform accurate experiments according to calculated flow rates. The two-way valves were located on the delivery lines after both pumps to stop back flow during bubble cleaning.

Both lines are pre-heated to the reaction temperature in separate pre-heaters to contact each other at reactor inlet. Reactor and pre-heaters were located inside an electric oven (AEW, Andover-Hampshire, England) with maximum heating temperature of 600^{o}C. It has an attached temperature controlling unit supported with a digital display (IPco, UK) that regulates the set-point temperature of up to 1^{o}C increment and shows the actual oven temperature. The organic pre-heater has a length of 6 m of 1/16 in SS-316 and the oxidant one is 12 m of 1/16 in SS-316 to ensure that all H_2O_2 will decompose to O_2. The lengths of pre-heaters were determined by modelling the needed heating surface that makes streams reach the reaction temperature, and also to decompose all H_2O_2 into O_2 and water (Croiset et al., 1997).

3.1.2 Reaction

First, organic and oxidant solution streams are mixed in a high pressure cross fitting (1/16", Swagelok, UK). Both streams enter the cross in an encountered flow configuration to provide an efficient mixing. The 1/16" tubular reactor and 1/16" type-K thermocouple were connected to the other ports of the cross and perpendicular to the flow direction. The reactor is made of SS-316 and has a length of 12.535 m and with an internal diameter of 0.6 mm and with internal volume of 3.544 ml. The 316 stainless steel was chosen as a construction material since there were no halogens used in all experiment feeds in addition to using a high continuous flow rates through small internal diameter that eliminates any risk of corrosion or plugging (Cutler et al., 1988). The continuous monitoring to the pressure indicator showed that the drop was minor where the variation was always ±3 bars from the desired operating pressure (250 bars) which ensure that the system was under isobaric condition. A grade 310 stainless steel thermocouple either at the

beginning or the end of the reactor was allowed to monitor and maintain the temperature during all experiments to be at the desired operating temperatures thus confirming isothermal status. The variation in all temperatures along the reactor was always around ± 3^{o}C compared to needed temperatures. The average of recorded temperatures was used as the reaction temperature. All thermocouples were linked to a 8 ports USB TC-08 thermocouple data logger (Picotech., UK) then to a PC computer with a data logging software installed to monitor real time temperatures around the reactor. After the reactor outlet the tubing continues to a shell and tube heat exchanger to cool reaction effluent then to depressurizing part of the system.

3.1.3 Depressurisation and Sampling

Once the effluent is cooled through heat exchanger, there is a pressure transducer (Druck, UK, Model PTX 521, 350 bars) that is fitted to the stream via tee connect and then linked to a digital-display pressure indicator (Druck, UK) to maintain the operating pressure during all runs. The pressure readings on pressure indicator were always similar to those on HPLC pump displays confirming reaching the desired operating pressure for all runs. Then the stream passes through a pressure release (relief) valve (Swagelok, UK, max 275 bars) that was attached as a safety precaution where the maximum pressure was always set at 265 bars. Then, the effluent continues through a back pressure regulator (BP66, Go regulators, USA, max 414 bars) that is used to maintain the pressure of the whole system according the needed operating pressure. After the BPR the effluent is expanded to ambient conditions and passed through a local modified gas/liquid separator that has a two-way valve at its bottom that when closed (at steady state) the liquid accumulate inside the separator while gas rises up and passes through an upper line that goes to gas sampling or flow measuring ports. The steady state of flow rate is determined by using a graduated cylinder and stopwatch with comparison to the calculated desired liquid flow

rates. A three-way valve is located at the end of the gas line so that when it is directed to gas sampling port via check valve the gas sample can be collected using a gas tight syringe (2.5 ml Fixed Luer Lock, SGE) to be analysed and when directed to the opposite port the gas flow rate is measured using a 50 ml manual soap-bubble flow meter (P/N: 20432, Sigma-Aldrich, UK) with assistance of stopwatch. After gas sampling and flow rate measure the accumulated liquid sample in the separator becomes enough to be collected and analysed by releasing the two-way valve at the bottom of the separator into a glass beaker.

3.2 Experimental procedure

3.2.1 Preparation of Reagents

Organic solutions

The investigated organic solutions in this work were DMF, DBU and ammonia. DMF solutions were prepared in the organic feed tank by diluting GC grade N,N-Dimethylformamide (Sigma-Aldrich, UK, >99 wt.%) in distilled water based on the required concentrations and with a normal mixing due to its complete solubility in water at ambient temperature. DBU solutions were prepared by diluting a reagent grade 1,8-Diazabicyclo [5.4.0] undec-7-ene (Sigma-Aldrich, UK, >99 wt.%) in distilled water to the needed concentrations. ammonia solutions were prepared by diluting ammonia hydroxide solution S.G 0.88 (Fisher Scientific, UK, 32.8 wt.%) in distilled water to the needed concentrations. For each experiment, a sample of each prepared original organic solution was collected to be analysed by TOC-5050A analyser and photometer (Spectroquant photometer NOVA60) to determine the initial concentration of TOC and total nitrogen respectively, before the destruction reaction.

Hydrogen peroxide solution

Aqueous hydrogen peroxide was chosen as a source of oxidant (oxygen) in all the experiments of this research. H_2O_2 is preferred in lab-scale continuous flow process as a source of oxygen rather than using directly other oxidants as molecular oxygen or air. Where the latter two require more cost due to the need for compressors in addition that it is hard to bring them into the contact with aqueous organic feed at the inlet of such tubular flow system. H_2O_2 is the best choice in our system since it is liquid and can be easily pumped through the system and mixed with organic solution at the reactor inlet (Lee et al., 1990). Also, here in this scale as a source of oxygen it is cheaper than O_2 or air. Simply, hydrogen peroxide thermally decomposes to oxygen when passes through pre-heater before entering the reactor. At large scales gaseous oxidants are the proper choice.

During the preparation of oxidant feed solution, a hydrogen peroxide solution (Sigma-Aldrich, UK, 35wt.% in H_2O) was used and diluted with distilled water according to the desired concentration (30 ml of 35 wt% H_2O_2 solution was always diluted in 2 litre of distilled water). The calculated flow rates of H_2O_2 for each experiment represent the amount of O_2 needed to oxidise the continuously introduced organic solution. In all runs, after preparation the diluted hydrogen peroxide solution in its feed tank is transferred to ice-bath to avoid any decomposition before entering the reactor.

3.2.2 Reactor Operation and Data Collection

Before starting every experiment, both HPLC pumps were operated by flowing distilled water and followed by cleaning bubbles in inlet tubes. Then, the system was pressurized using back pressure regulator until it stabilised at 250 bars. Then, to reach the desired operating temperature the electric oven was turned on that usually requires from 45 minutes to one hour. During pre-heating the system the flow rates on both pumps were adjusted to be similar to the

flow rates of first reaction time to stabilise the temperature faster. When the operating temperature and pressure are reached the set points and stabilised by monitoring thermocouple data logging software and transducer pressure indicator, quickly both pumps were turned off and all pump feed lines were switched to the already prepared organic and oxidant feed solutions. Then, both pumps were turned on. After this step the oxidation reaction started. Then, usually from 20 to 30 minutes are required to obtain steady flow rates and stable temperatures after the reaction start. To ensure that steady-state is obtained during the reaction, the total produced liquid flow rate was measured every 5 minutes from the reaction start using graduated cylinder and stopwatch and compared to the calculated flow rate. When this state was confirmed the gas sample was collected twice at the gas sampling port using a gas tight syringe followed by measuring the produced gas flow rate using the bubble flow-meter and stopwatch. Immediately the gas sample was injected to the GC system (GC-6890N, Agilent) to analyse the gaseous products. Meanwhile, the liquid samples were collected at the bottom of separator using clean and secure vials to be analysed for TOC and nitrogenous analysis. During all runs the temperature and pressure readings from data logging software and pressure indicator and pump display were always monitored and recorded continuously.

At the end of each experiment, a sample of the original organic solution was collected to be analysed along with other reaction liquid samples. After finishing all measurements and samplings the operating conditions can be altered in order to perform another experiment or the system can be cooled, depressurized and shut down.

3.3 Analytical Methods

It is essential to quantify the gaseous and liquid phase products in a study includes the oxidation of carbon and nitrogen contents. This enables to assess the process destruction efficiency and to quantify and follow the speciation of carbon and nitrogen products at the studied conditions. In addition, to obtained the kinetic data. The used analytical techniques to quantify liquid and gaseous products are shown in Table 7.

During this study, the available GC system (GC-6890N, Agilent, USA) that supported with a CTR I concentric column was used to analyse gaseous-phase products of all experiment samples. Liquid-phase analysis for reaction effluent was carried out using a total organic carbon analyser (TOC-5050A, Shimadzu, Japan) for carbon content and a photometer (Spectroquant® Nova 60 photometer, Merck, Germany) for nitrogenous species. The descriptions of all analytical methods employed are illustrated in subsequent sections.

Table 7: Quantified liquid and gaseous species and used corresponding analytical techniques.

Phase	Content	Quantified Species	Analytical Technique
Liquid Phase	Carbon content	Total Carbon (TC)	TOC Analyser
		Inorganic Carbon (IC)	TOC Analyser
		Total Organic Carbon (TOC)	TOC Analyser
	Nitrogen content	Total Nitrogen (TN)	Spectrophotometric cell test kit
		Ammonium Ion (NH4)	Spectrophotometric cell test kit
		Nitrate Ion (NO_3^-)	Spectrophotometric cell test kit
		Nitrite Ion (NO_2^-)	Spectrophotometric cell test kit
Gaseous Phase	Carbon content	Carbon Dioxide (CO_2)	GC-TCD
		Carbon Monoxide (CO)	GC-TCD
		Methane (CH_4)	GC-TCD
	Nitrogen content	Nitrogen Gas (N_2)	GC-TCD

Remarks*:* TOC- total organic carbon

GC- gas chromatography

TCD- thermal conductivity detector

3.3.1 Gas-Phase Analysis

The gas-phase samples were analysed during each run using a GC system (GC-6890N, Agilent, USA) that supported with a thermal conductivity detector (TCD) and CTR I concentric column (6'×1/4' outer & 6'×1/8' inner SS column, P/N: 8700, Alltech, UK). Simply, the GC the gas sample was taken by the carrier gas into the column inlet to be rapidly evaporated then all gas components travel through the column at certain rates based on their partition between two phases. At the end of the column the detector generates a signal that represents the concentration

of each gas component based on its retention time and this signal was displayed on a chromatogram.

In this study, simply when the GC becomes ready, 2.5 ml of gas sample was injected twice through a 2 ml injection loop (needed injection volume: 2µl) then into the column. The detected gases were CO_2, O_2, N_2 and CO. Before using the GC equipment it was calibrated using a standard gas mixture that contains all the possible gaseous products from SCWO of nitrogen-containing compounds. The standard gas mixture (1.55 L 112DA standard gas, STG, UK) consists of 1% CO_2, 1% CO, 1% O_2, 1% N_2, 1% CH_4, 1% H_2 and balance of Helium. After each GC analysis (15 mins) the obtained area under curve (AUC) for each gas component was referred to its corresponding AUC from standard gas mixture. Then, since the percentage (molar fractions) of each gas component in the standard gas was known, the following formula was used to calculate the concentration for each detected gas.

$$Gas\ i\ vol\% = \left(\frac{AUCi \times 1\%}{AUC,standard}\right) \times 100 \qquad (3.1)$$

Even though the gas samples were directly transferred from the rig to GC equipment using a tight-gas syringe for all experiments, it was noticed that a large amount of air was always mixed with all gas samples due the unreliable way of gas sampling (rig design) where the volume% and yield of N_2 were always high. In addition, other challenges such as non-secure injection inlet, inlet valve leak and contaminated column hardened obtaining accurate results for gaseous phase products.

Table 8 shows the major operating conditions that used to develop the GC analysis method. Figure 12 shows the typical chromatogram that can be produced and the gas sequence on this type of columns.

Table 8: GC-TCD operating parameters used during all gaseous analysis.

Carrier gas	
Carrier Gas	Pure Helium
Flow rate (via column)	65 ml/min
Injection	
Injection (front inlet) Temperature	50^{o}C
Loading Time	0.5 min
Run Time	15 minutes
Detector conditions	
Detector Type	TCD
Detector Operating Temperature	250^{o}C
Reference Gas	Helium
Reference Gas Flow rate	65 ml/min
Oven	
Equilibrium Time	1 minute
Oven Temperature set-point	33^{o}C

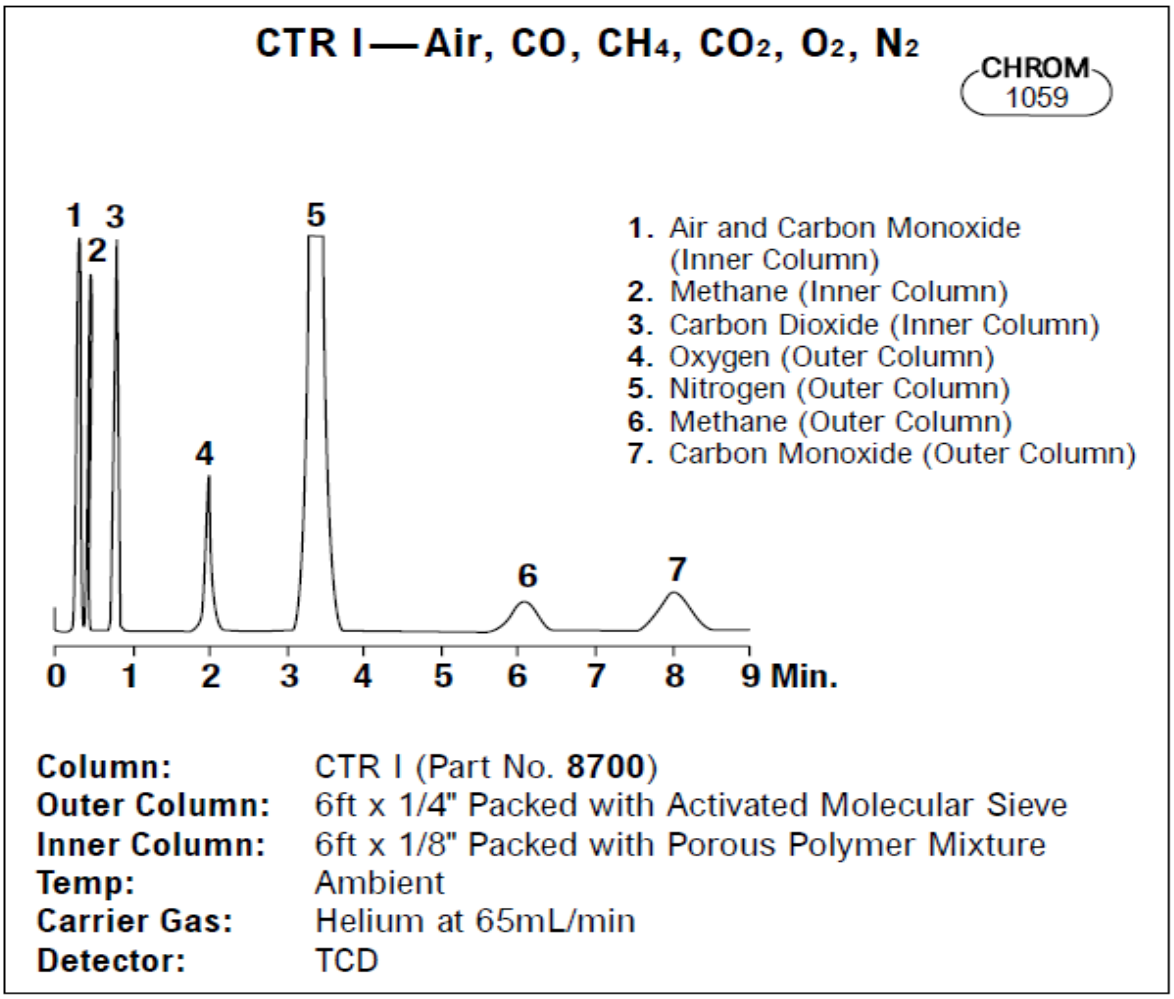


Figure 12: Typical gas-phase chromatogram on CTR I column (Alltech UK, 2012).

3.3.2 Liquid –Phase Analysis

3.3.2.1 DMF, DBU and Ammonia Experiments

The samples of DM, DBU and ammonia feed solutions and liquid-phase products were usually directly analysed or after being refrigerated for around a week as maximum. This study aims to focus on SCWO destruction and kinetics of selected organic compounds rather than identifying the intermediates and thus proposing the reaction pathways. Therefore, the analysis of all liquid samples focused on using TOC analysis and photometer that were enough tools to know

the total organic carbon and total nitrogen removal in addition to the yields of nitrogen species. It is worth mentioning that quantified TOC here will cover the carbon content from IPA as well.

3.3.2.1.1 Total Organic Carbon Analysis

Total organic carbon (TOC) represents the carbon content that bound to the organic compound, thus knowing the converted TOC from the organic feed enables to assess the destruction efficiency of TOC and thus SCWO process at studied conditions. In this work, all samples were analysed using the available TOC analyser (Model TOC-5050A, Shimadzu, Japan). The analyser is attached to an auto-sampler (ASI-5000A, Shimadzu, Japan) and linked to a PC-screen that supported with a TOC-Control software that facilitates to set up for samples on the auto-sampler and then to perform the whole analysis process. The operation of this analyser is based on the combustion/non-dispersive infrared gas analysis method that widely used for TOC measurement (Shimadzu, 2001). This analyser measures the total carbon (TC) and inorganic carbon (IC) contents of liquid-phase effluents and the organic feed and then automatically determines the TOC by subtracting IC from TC. IC represents all inorganic carbon in form of carbonates and hydrogen carbonates generated from the reaction.

Simply, the carrier gas (pure air) is introduced to the machine and passes through a TC combustion tube that filled with TC catalyst and heated by an oven up to 680^{o}C. Then, samples are injected via injection line to the combustion tube so that TC content in the sample is combusted and decomposes to CO_2. Then, the carrier gas takes CO_2 through an IC reaction vessel to be cooled and dried by a dehumidifier. It is then passed via a halogen scrubber to a non-dispersive infrared gas analyser (NDIR) where CO_2 is detected and measured. Lastly, TOC can be determined by subtracting IC from TC (TC=TOC+IC). Thus, the TOC removal can be calculated as explained in equation 3.5 in page 111.

3.3.2.1.2 Spectrophotometric Analysis

The nitrogenous species in the liquid effluent such as ammonia, nitrite, nitrate and total nitrogen (TN) need to be quantified in order to assess N oxidation from the SCWO of organic feed. This would help to evaluate the reduction in ammonia, the removal of TN and the behaviour of other species. The used nitrogenous analysis in this study consists of Spectrophotometric Cell Tests (Merck, VWR International Ltd, UK) that included test tubes and reagents for each nitro-specie test and Spectroquant® NOVA 60 photometer (Merck, VWR international Ltd, UK). Spectrophotometry is a quantitative measurement to the intensity of light that the substance absorbs by passing a light via the sample. Adding a reagent to the sample during this analysis create a colour that allows for the machine to compare the light intensity of the colour with the intensity of a standard one, and thus the concentration of targeted nitrogenous species can be measured.

In this study, the analysis of each nitrogenous component was carried out according to the provided procedures (Merck, 2012) as briefly described in the subsequent sections. Simply, for each analysis a certain amount of the reagent or reagent mixture was added to the liquid effluent sample and after a specific reaction inside each cell test and obtaining a certain colour, the tube was taken to the spectroquant NOVA 60 photometer that directly measures and displays the concentration. The readings were taken 5 times for each analysis.

In this work, due to the high cost of cell tests, only one analysis (for each component) was carried out for each experiment at 6 seconds of residence time. This time was selected as most of oxidation occurred and also to avoid laminar flow regime that possible at longer residence times. The calibration of the photometer was electronically stored and regularly checked.

- Total Nitrogen (TN) measurement

According to Koroleff's method, organic and inorganic nitrogen compounds are converted into nitrate when treated with an oxidizing agent in a thermoreactor. In a solution acidified with sulfuric and phosphoric acid, this nitrate reacts with 2,6-dimethylphenol (DMP) to form orange-coloured 4-nitro-2,6-dimethylphenol that is measured photometrically.

The TN analysis procedure was as follows: pipetting 1ml of the sample into an empty cell and 9 ml of distilled water was added and mixed. Then, 1 level micro-spoon of reagent N-1K was added and mixed to be followed by adding 6 drops of reagent N-2K and mixed. The mixture in the cell was heated for an hour at 120^{o}C on a calibrated multi-Blok heater (model 2050-1, Lab-line instruments, UK). Then, the cell was kept to cool down to room temperature. Then, 1ml of reagent N-3K was added to 1ml of cooled sample in a new reaction cell followed by mixing and kept stand for 10 minutes. Lastly, the cell was analysed (5 readings) on Spectroqaunt NOVA 60 photometer to obtain the concentration of TN. Thus, TN removal can be determined as explained in equation 3.6 in page 111.

- Ammonium Ion measurement

Ammonium nitrogen (NH_4-N) occurs partly in form of ammonium ions and partly as ammonia based on the pH equilibrium between the two forms. In strongly alkaline solution ammonium nitrogen is present almost entirely as ammonia, which reacts with hypochlorite ions to form monochloramine. This in turn reacts with a substituted phenol to form a blue indophenol derivative in which its concentration can be determined photometrically.

The ammonium analysis procedure was as follows: pipetting 0.1ml of the sample into a reaction cell (contains alkaline solution) that was closed and mixed. Then, one dose of reagent

NH_4-1K was added, where the cell was closed and effectively mixed until the reagent was completely dissolved. The cell was kept on the rack for 15 minutes, and then it was measured in the photometer to obtain ammonium ion concentration. Afterwards, the yield of produced ammonium ion can be calculated as shown in equation 3.7 in page 111.

- Nitrite Ion measurement

In the acidic solution nitrite ions (NO_2^-) react with sulfanilic acid to form a diazonium salt, which in turn reacts with N-(1-naphthyl) ethylenediamine dihydrochloride to form a red-violet azo dye. This dye then is determined photometrically. The procedure of nitrite analysis was as follows: pipetting 5.0 ml of the sample into the reaction cell, and then it was closed and vigorously shaken until the reagent was completely dissolved. After 10 minutes of reaction time the cell was measured in the photometer. Afterwards, the yield of nitrite was determined according to equation 3.8 in page 111.

- Nitrate Ion measurement

In a solution acidified with sulfuric and phosphoric acid, nitrate ions (NO_3^-) react with 2,6-dimethylphenol (DMP) to form orange-coloured 4-nitro-2,6-dimethylphenol, the concentration was determined photometrically.

The procedure of nitrate analysis was as follows: pipetting 0.50 ml of the sample into a reaction cell without mixing. Then, a 1.0 ml of reagent NO_3-1K was pipetted and then the cell was closed and mixed. The hot cell was kept standing for 10 minutes reaction time before it was measured in the photometer. The yield of nitrate was determined as shown in equation 3.9 in page 111.

3.3.2.2 Oxidant feed analysis

There was no separate analysis technique for the prepared hydrogen peroxide solutions for all experiments. Since there is no TOC or TN in H_2O_2 feed to be evaluated and also since it is known how much H_2O_2 was prepared according the calculations and then how much O_2 needed. H_2O_2 was used as a source of oxidant where it decomposes in the preheater to generate the needed O_2 in addition to the water according to the following reaction equation:

$$H_2O_2 \rightarrow \frac{1}{2}O_2 + H_2O \qquad (3.2)$$

According to the molar ration from previous reaction equation, the concentration of O_2 was determined as it was a half of H_2O_2 concentration.

3.4 Data Analysis

During all runs the experimental measurements and analytical results were used to assess the process destruction efficiency via TOC removal, TN removal and ammonia removal in addition to kinetic parameters. For all experiments, temperature and pressure measurements that guaranteed all runs were performed under supercritical conditions were recorded. Temperatures along the reactor were maintained to be ± 3^{o}C and pressures were ± 5 bars from their set-points. Also, all the measurements of gas and liquid phases for reaction effluents or organic feed were carried out and analysed according to the previously explained procedure in analytical method part. Also, the average of these measurements and results for each experiment was used to determine the following:

- Volumetric flowrates at the desired reaction conditions.
- Pressure stability to ensure reaching isobaric conditions during each run.

- Temperature stability to ensure reaching isothermal conditions during each run.
- Liquid flow velocity and Reynolds number (Re) based on selected residence times to verify having turbulent flow during all runs.
- TOC removal from reactants (organic and IPA).
- Concentration of nitrogenous species of reaction effluent (using spectrophotometry).

A steady-state check experiment was carried out before each set of experiments at fixed conditions including the residence time where the TOC results were very similar to each other. This confirmed that all experiments were carried at steady-state status. TOC results showed that the associated error (percent error) was always less than ± 4% based on TOC_o that obtained with all experiments.

3.4.1 Calculated Parameters

3.4.1.1 Reactant Concentrations at Reactor Inlet and Feed Preparation

Measuring the concentrations of organic feed and reaction effluent was carried out as explained previously in the analytical methods. Before each set of experiments, a series of calculations were performed in order to run well-calculated reactant amounts and for further analytical calculation. First, the molar concentration of organic compound at the inlet of reactor and at the supercritical conditions was selected, where then based on reaction molar ratios it was calculated for IPA and O_2. Then, ambient concentrations of organic material, IPA and O_2 were calculated. It is worth mentioning that water densities at SC and ambient were used here due to the fact that most of prepared solutions consist of water (up to 99.2% water as minimum) in addition to that there is no scientific data for organic-water-oxygen mixtures. Water properties were obtained from the thermophysical properties of fluid system (NIST). Afterwards, volumes of needed organic and IPA were calculated in order to prepare 1L solution as well as H_2O_2

amount that needed to oxidize 1ml of the organic solution (30ml of H_2O_2 dissolved in 2L distilled water, oxidant feed). Then, flow rates at supercritical conditions (reactor inlet) were calculated from reactor volume and selected residence times followed by those of organic and oxidant at ambient conditions. Moreover, Reynolds number (Re) was calculated to ensure having turbulent flow for all reactants inside the PFR. Lastly, the concentration of total organic carbon (TOC_o) and total nitrogen (TN_o) in the feed was calculated in order determine the removals, associated error and also to check the need for dilution before each analysis.

3.4.1.2 Volumetric Flowrates and Other Calculated Parameters

Since the residence times (2-10 seconds) for all the experiments of this work were selected in advance, the total volumetric flowrates at reactor inlet (at supercritical conditions) were calculated by dividing reactor volume (V) by residence time (Tr) as shown below:

$$v = \frac{\mathrm{V}}{\mathrm{Tr}} \tag{3.3}$$

The stoichiometric amount of oxidant to organic can be defined as:

$$SR = \frac{([oxidant/organic])actual}{([oxidant/organic])stoich} \tag{3.4}$$

Where if SR=1 this indicates that exactly the needed amount of oxygen is supplied, if SR < 1 this means less than what is needed for reactants is supplied and if SR > 1 this indicates that there is excess of oxygen in the system.

TOC removal that represents the conversion of starting organics and determines the process destruction efficiency at each analysis was determined from the measured TOC concentrations of

original organic solution (TOC_o) and reaction effluent (TOC_f) at any residence time according to the following equation:

$$\text{TOC Removal \%} = \left(\frac{\text{TOCo} - \text{TOCf}}{\text{TOCo}}\right) \times 100 \qquad (3.5)$$

Also, TN removal that represents the conversion of organic nitrogen in the feed can be determined from the measured TN of original solution (TN_o) and reaction effluent (TN_f) at any reaction time using the following equation:

$$\text{TN Removal \%} = \left(\frac{\text{TN}o - \text{TN}_f}{\text{TN}o}\right) \times 100 \qquad (3.6)$$

The yields of produced ammonium ion, nitrite and nitrate can be calculated from equations 3.7, 3.8 and 3.9 respectively as shown below:

$$\%\, NH_4\ yield = \frac{\frac{mg}{l} of\ NH4 \times \frac{no\ of\ N\ atoms\ in\ NH4}{Mw\ NH4\ (\frac{mg}{mmol})} \times total\ flow\ rate}{\frac{mg}{l} of\ feed \times \frac{no\ of\ N\ atoms\ in\ feed}{Mw\ of\ feed\ (\frac{mg}{mmol})} \times feed\ flow\ rate} \times 100 \qquad (3.7)$$

$$\%\, NO_2\ yield = \frac{\frac{mg}{l} of\ NO2 \times \frac{no\ of\ N\ atoms\ in\ NO2}{Mw\ NO2\ (\frac{mg}{mmol})} \times total\ flow\ rate}{\frac{mg}{l} of\ feed \times \frac{no\ of\ N\ atoms\ in\ feed}{Mw\ of\ feed\ (\frac{mg}{mmol})} \times feed\ flow\ rate} \times 100 \qquad (3.8)$$

$$\%\, NO_3\ yield = \frac{\frac{mg}{l} of\ NO3 \times \frac{no\ of\ N\ atoms\ in\ NO3}{Mw\ NO3\ (\frac{mg}{mmol})} \times total\ flow\ rate}{\frac{mg}{l} of\ feed \times \frac{no\ of\ N\ atoms\ in\ feed}{Mw\ of\ feed\ (\frac{mg}{mmol})} \times feed\ flow\ rate} \times 100 \qquad (3.9)$$

3.5 Process Hazard Analysis

In general, operating under high temperatures and high pressures made SCWO a relatively hazardous system that needs certain care and handling during operation. Burns due to exposure to hot surfaces is another associated hazard. Over pressurisation or pressure drop during run could cause serious problems when it occurs. In addition, exposure to toxic chemicals either by skin or eye contact or even by inhalation could harm the operator health. Lastly, a proper power supply and safe electric connections are needed to avoid any electric shocks. Chemical hazard and risk assessment illustrated these possible hazards and the measures that were considered during operation. To mitigate these hazards and work in safe environment carful procedures were implemented during all experiments.

Toxic Chemical Exposure

To minimise the exposure risk of organic materials and reaction effluent, a proper protective lab clothing, masks and gloves were always used during preparation and handling. Also, a fume cupboard was always used during solution preparation and to vent volatile components. After each experiment and analysis the remained original solution and liquid reaction effluents were always disposed according to the lab safety procedure. A flexible ventilator that fitted around the rig always guaranteed that no presence for CO from gas effluent during experiments.

Over Pressurization and Pressure Drop

Over pressurization risk was mitigated by a continuous monitoring to the pressure during all runs. Also, a pressure safety valve was linked to the rig and set at 265 bars. Any pressure drop was considered to avoid system leakage.

Hot Surface Burns

Electric oven door was always kept tightly closed and with secure seal during all runs. Also, 'hot surface' sign was posted on the oven door. Also, to minimise the risk all hot tubes that come from oven and the heat exchanger were kept behind a protective transparent shield. A special protective gloves were always used to open the oven or when dealing with hot parts.

Electric Shocks

To avoid electric shocks equipment such as HPLC pumps, oven, temperature controller and pressure indicator were placed on proper surfaces and connected to separate power sockets.

RESULTS AND DISCUSSION

The experimental results of this work are presented in four chapters, which consist of the results and their discussion section. Every chapter is designated for the treatment of a specific material. Chapter 4 covers the effect of SCWO system operating variables on DMF removal in the presence of co-fuel in addition to the reaction kinetics. Chapter 5 and 6 study the SCWO of DBU in the absence and presence of co-fuel and ended with the kinetics analysis. Lastly, chapter 7 investigates the performance for SCWO of ammonia in the presence of co-fuel.

CHAPTER 4 - SUPERCRITICAL WATER OXIDATION OF N, N-DIMETHYLFORMAMIDE (DMF) IN THE PRESENCE OF ISOPROPYL ALCOHOL (IPA) AS A CO-FUEL

4.1 Introduction

In order to examine SCWO as a promising method of toxic wastewater treatment and to bring it as a more efficient process to the market, it is necessary to fully understand destruction behaviour and oxidation kinetics especially with dilute nitrogen-containing wastewaters in this process. For these reasons, this study aims to investigate the effect of adding co-fuel associated with the effects of various process operating variables on DMF treatability.

This chapter displays the results and their discussion for the experiments that were performed to study the supercritical water oxidation of DMF in the presence of isopropyl alcohol (IPA) as a novel approach to study its effect on the process improvement and DMF removal compared with IPA free system. This was associated with investigating the effect of the typical operating conditions on the destruction of DMF such as temperature, initial concentration of organic compound, initial concentration of the co-fuel, oxidant amount in addition to residence time.

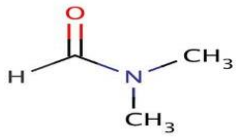
Moreover, the behaviour of ammonia yield as an unwanted intermediate from DMF oxidation was also investigated in the presence of IPA. Finally, kinetic analysis of DMF oxidation was also carried out and presented in this part including the evaluation of co-fuel effect on Arrhenius parameters and reaction temperature. The main parameters that were used in this work to show the performance of the process under studied conditions were total organic carbon removal (%TOC removal), total nitrogen removal (%TN removal) and yield of ammonia (%NH_4).

4.2 DMF Selection

DMF is a simple amide with the molecular formula of (C_3H_7NO). It consists of double methyl-substitutes on the amide group and represents a general class of simple nitro-aliphatic compounds. DMF is commonly used as a solvent in numerous applications in industry. For example, it is widely found in the synthesis of acrylic fibres, polymers, surface coatings and vinyl films as a spinning solvent. Also, due to its catalytic properties it is employed as a reaction medium in pharmaceutical and chemical synthesis (EPA, 2000). Moreover, it is used as a purification and separation solvent in the formulation of adhesives, pesticides, paintings, dyes, resins, epoxy, petroleum products, acetylene, aliphatic hydrocarbons and pharmaceuticals (WHO, 2001).

The physical properties of DMF are illustrated in Table 9. DMF as a colourless and odourless liquid was completely miscible with water in all proportions that facilitated to the homogeneity of prepared organic solutions and prevented any precipitation at room conditions during all runs.

Table 9: Physical properties of DMF (Chembook, 2016).

DMF , CAS number: 68-12-2	
Structure	
Molecular formula	C_3H_7NO
Appearance and solubility	Colourless liquid, miscible with water in all proportions and in the majority of organic liquids.
Molar mass	73.09 g/mole
Density	0.944 g/ml
Viscosity	0.92 cp (20^{o}C), close to H_20
Boiling point	153^{o}C
Melting point	60^{o}C

The reasons of selecting DMF as a model compound in this study are listed below:

- DMF is widely available hazardous pollutant in pharmaceutical and other numerous wastewater streams in industry. Thus, the investigation of the SCWO of DMF would enrich the field of the SCWO technology applicability to treat DMF as a start to more general class of N-containing compounds that are of high interest due to their refractory nature, yet are not widely researched.
- DMF is a simple aliphatic compound. Its SCWO study would facilitate the assessment of its reactive behaviour and reaction kinetics and therefore the results would provide to compare this class of N-containing organics to more complex nitrogenous compounds as in case of DBU in Chapter 5.
- Early SCWO studies on DMF were undertaken by MODAR Inc. and have shown its treatability (Thomason et al., 1990). However, further studies are still needed to enrich the

collective knowledge of DMF. Thus, IPA as a co-fuel is used in this study to enhance further DMF destruction behaviour and kinetics. Moreover, adding IPA will examine the potential to oxidise ammonia as unwanted non-biodegradable intermediate and to reduce SCWO system operating temperatures. The stoichiometric equations for the complete oxidation of DMF in SCWO system in the presence or absence of IPA and in addition to the decomposition of hydrogen peroxide are shown below:

$$C_3H_7NO + 4.25\ O_2 \rightarrow 3\ CO_2 + \frac{7}{2}\ H_2O + \frac{1}{2}\ N_2 \quad (4.1)$$

$$C_3H_7NO + C_3H_8O + \frac{35}{4} O_2 \rightarrow 6\ CO_2 + \frac{15}{2}\ H_2O + \frac{1}{2}\ N_2 \quad (4.2)$$

$$H_2O_2 \rightarrow \frac{1}{2} O_2 + H_2O \quad (4.3)$$

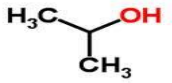
4.3 IPA Selection

Isopropyl alcohol (C_3H_8O) is the simplest form of secondary alcohols. It is miscible with water and a majority of organic liquids and has suitable physical properties as shown in Table 10. It has numerous applications in industry. For example, it is widely used as a solvent for coatings, industrial manufacturing and as a cleaning liquid. IPA is particularly preferred for pharmaceutical applications due to its low toxicity. In SCWO technology, IPA has obtained more interest by several researchers as a co-fuel (Cocero et al., 2000a, Bermejo et al., 2008). As explained in Section 2.7.5, co-fuels (as alcohols) in SCWO generate extra heat due to their high calorific value, rapidly react and enhance the production of free radicals that all would improve the destruction of treated material and thus improves the process efficiency. Also, it is anticipated to reduce the activation energy and needed operating temperatures. Moreover, co-fuels have not

been used with SCWO of DMF so far. Therefore, IPA was selected in study. In this work, in addition to previously mentioned advantages, IPA as a co-fuel was selected as opposed to other known alcohols such as methanol and ethanol for several reasons as listed below:

A. Greener alcohol: IPA is relatively not toxic solvent either in research or in industrial usage compared with other organic solvents where it is widely used in pharmaceutical industry. Also, IPA can be separated from aqueous solutions by adding salts, NaCl, since it is insoluble in salt solutions while other organic solvents are hard to separate them easily.
B. Efficiency: IPA as a co-fuel is widely preferred than other co-fuels as enhancer for oxidation reaction in SCWO process. It has been reported that Me-OH achieved 40% NH_4 removal and ethanol achieved up to 100% NH_4 removal when ammonia treated as a starting material (Webley et al., 1991, Ploeger et al., 2007). However, IPA is expected to have more efficiency than ethanol to treat organic compounds in addition to reduce ammonia as an intermediate. As a solvent IPA and ethanol have similar effect but in this study IPA is selected due to its other properties.
C. Dissolving organics: IPA dissolves a wide range of non-polar organics at ambient temperature, thus aiding in pre-treatment of aqueous waste streams. It is less volatile than ethanol and an effective solvent at any concentration. Ethanol is used at 70wt% solution where above this concentration it evaporates quickly and less than 70wt% becomes not effective solvent.
D. Peroxide feature: IPA is organic peroxide (ROOR) that breaks to form free radicals (reactive in serial reaction).
E. Economic view: IPA is slightly cheaper than ethanol.

Table 10: Physical properties of IPA (Chembook, 2016).

IPA , CAS number: 67-63-0	
Structure	
Molecular formula	C_3H_8O
Appearance and solubility	Colourless liquid, miscible with water and in the majority of organic liquids.
Molar mass	60.1 g/mole
Density	0.786 g/ml (20^{o}C)
Viscosity	1.96 cp (25^{o}C)
Boiling point	82.6^{o}C
Melting point	-89^{o}C

In summary, DMF as a chemically stable (non-biodegradable in nature) nitrogenous compound and IPA were selected upon the previously mentioned reasons to conduct further study using SCWO technology as an alternative process to treat such hazardous material. The results from this work are expected to give in depth knowledge about DMF destruction behaviour and its reaction kinetics in presence of IPA that would allow for more understanding to the destruction of a wider range of hazardous materials and would help in the comparative study with the next more complex material, DBU), as in Chapter 5.

4.4 Effect of System Operating Conditions

SCWO Process diagram, components and experimental procedures used in this chapter were previously described in Sections 3.1 and 3.2.

4.4.1 Experimental Work Plan

In this work, the SCWO of DMF in solutions with water and the presence of IPA was carried out at various temperatures, DMF feed concentrations, IPA concentrations, oxidant ratios and residence times. For each individual variable studied, a temperature of 400^{o}C, 10 mM of DMF solution and 10 mM of IPA (all at SC conditions) and delivering the needed stoichiometric oxidant ratio (1 SR) were used as minimal values to avoid effect overlapping. Pressure was fixed at 250 bars in all runs as it has been widely reported that it has no effect on the process efficiency in supercritical region except maintaining mono-phase system (Al-Duri et al., 2008).

The ranges of all used operating conditions during this part were summarized in Table 11. Also, the justifications for selected ranges for every individual operating variable are explained in the subsequent sections.

Table 11: Summary of the operating conditions used in SCWO of DMF experiments.

Variable	Range	Fixed conditions
Temperature	400 - 525 ^{o}C	$[DMF]_o$ = 10 mM $[IPA]_o$ = 10 mM SR = 1SR
$[DMF]_o$	1-20 mM	Temp = 400 ^{o}C $[IPA]_o$ = 1-20mM, IPA/DMF ratio=1 SR = 1SR
$[IPA]_o$	1-30 mM	Temp = 400 ^{o}C $[DMF]_o$ = 10 mM SR = 1SR

		Temp = 400 ^{o}C
Oxygen ratio	0.8 – 2 SR	$[DMF]_o$ = 10mM
		$[IPA]_o$ = 10Mm
Residence time: 2-10 seconds for all experiments, and Pressure of 250 bars.		

4.4.2 Effect of Residence Time

The investigated range of residence times was selected to be from 2 to 10 seconds in all runs, where the maximum residence time of 10 seconds was to maintain the turbulent flow regime through the reactor and the minimum of 2 seconds was based on the ultimate flow rates the HPLC pumps can deliver. Also, this relies also on the other conditions used such as temperatures, oxidant ratios and organic concentrations. During all runs, stabilisation time of 25-30 minutes was adequate to confirm obtaining accurate residence times as experiments were designed. In addition, steady state check before each chapter confirmed this. The effect of residence time on DMF oxidation (via TOC removal) was studied and as shown in Figure 13.

Generally, Figure 13 shows a clear increase in TOC removal of DMF with all residence times over temperatures investigated. Expectedly, longer reaction time allowed for more contact between organic matter and oxidant and thus for further oxidation. Effect of residence time on TOC removal almost followed the same pattern with all temperatures investigated (in the presence of IPA). Its effect was slightly sharper with baseline experiment due to IPA absence. There was a considerable TOC removal during the early stages of oxidation reaction, which confirms that most oxidation takes place at the reactor's front section. For example, at 400^{o}C the TOC removal was 85.7% after 2 s. This agrees with another study that showed most of TOC removal occurred at reactor entry and during the first 2 seconds (Cabeza et al., 2011). This is due to the high solubility of reactants in SCW and high temperatures that makes SCWO process very

rapid where most of oxidation occurs in the early stages of reaction. Moreover, the graph shows no significant improvement in the removal at late stages as from 6 s to 10 s (this can be seen also in Figure 14) indicating no need for using a bigger reactor to improve the oxidation efficiency as other conditions could be exploited at the same range of residence times studied in this work. Also, from engineering point of view, bigger system leads to more cost and control issues.

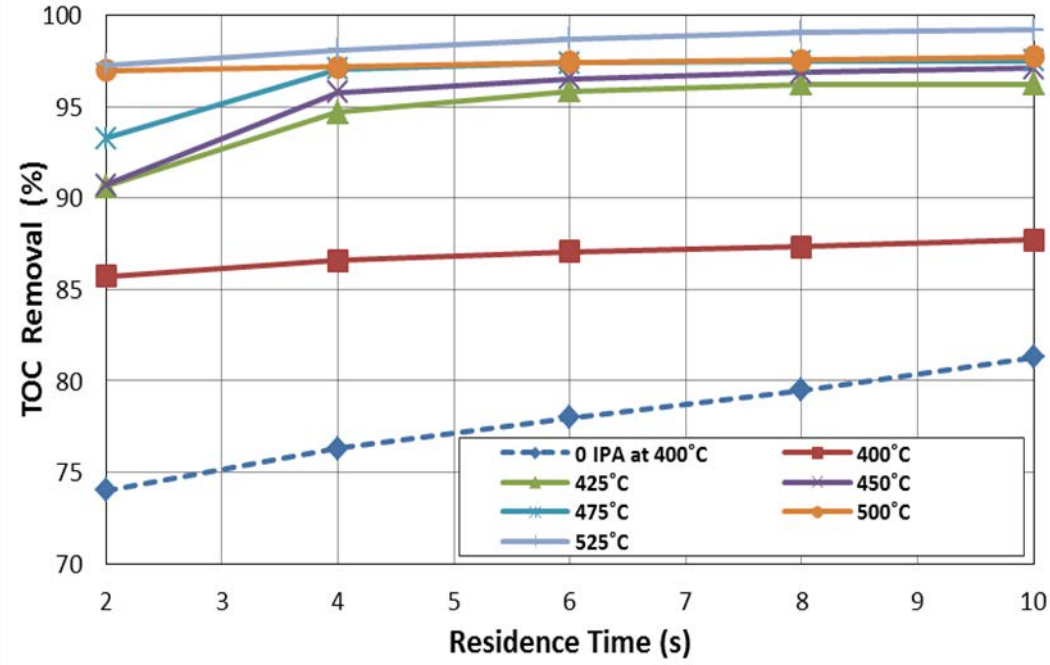


Figure 13: TOC removal against residence time at various temperatures. At 10 mM DMF, 1IPA/DMF ratio, SR of 1, 250 bar and also at 0 IPA.

4.4.3 Effect of Operating Temperature

The effect of temperature on SCWO of DMF was investigated in the range from 400 to 525^{o}C at initial DMF concentration of 10 mM, 1 IPA/DMF ratio, 1 SR, 250 bar and residence time from 2 to 10 s. Due to the significant effect of temperature on oxidation reaction and reaction kinetic parameters of chemical species involved in DMF treatment, this wider range of operating temperatures with a 25^{o}C increment was selected and it was within the typical

temperature ranges found in the literature. Choosing a minimum of 400°C confirmed that the medium was always above the critical point (in mono-phase) in all runs, while a maximum temperature of 525°C was upon the ultimate heating capacity of the oven used in these experiments.

Figures 14 and 13 show the significant effect of temperature on TOC removal especially in the presence of IPA when compared to non-IPA experiment at different residence times. Here one baseline experiment for this set was conducted at 400°C without IPA and at same other conditions.

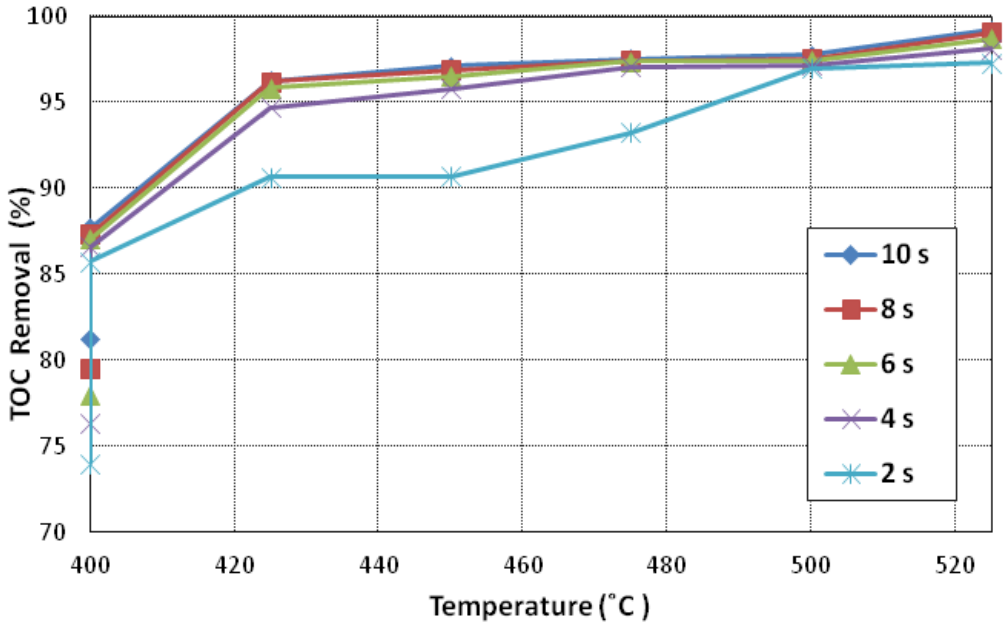


Figure 14: Effect of operating temperature on TOC removal at 10 mM DMF, 1IPA/DMF ratio, SR of 1, 250 bar and various residence times.

Combining both graphs shows clearly that temperature has a significant effect on the oxidation efficiency of organics. The positive role of temperature on the removal was obvious from the TOC removal enhancement. For instance, the TOC removal increased from 87.7% at 400°C to 99.2% at 525°C after 10 s of residence time, which is the maximum promising removal

obtained in this work. These results are in accordance with other works that observed increasing temperature enhanced the TOC removal and that temperature is the most influential factor on the oxidation of organics (Cocero et al., 2000a, Bermejo et al., 2008). Besides, this significant removal due to the essential role of temperature, adding IPA as an auxiliary fuel clearly enhanced the destruction compared to non-IPA experiments. For example, both figures show when IPA added the TOC removal obviously increased by 16% to reach 85.7% at 2 s and by 8% to reach 87.7% at 10 s at the same lower temperature of 400^{o}C. The existence of IPA enhanced the role of temperature via excess heat generated and thus more molecular collision. IPA also generates more free radicals and oxidises rapidly. Also, with the presence of IPA and at relatively lower temperature such as 500^{o}C a high TOC removal of 97.7% was obtained at 10 s, which can be attributed to the role of IPA in addition to the relative simple structure of DMF.

Moreover, in the presence of IPA, both figures show a lower TOC removal of 85.7% (@ 2 s) and 87.7% (@10 s) at 400^{o}C compared to the rest of temperatures, where this is due to relative closure of 400^{o}C to the critical point of pure water (i.e 374^{o}C) while free radical generation enhances significantly at higher temperatures.

Based upon that, it is anticipated that temperatures of 500^{o}C or 525^{o}C could be enough to achieve a complete TOC removal by slightly elevating other conditions such as adding more co-fuel, oxidant, organic or even longer residence time rather than increasing the temperature. In this work, the enhancement in the role of temperature as the most influential factor was only with using 10 mM of IPA, thus it is expected that addition of more IPA would significantly enhance the system performance and also with elevating other variables the role of IPA would be more dominant.

Furthermore, it is obvious in this work that adding IPA as an enhancer lowered the needed operating temperatures to treat DMF and thus this would improve SCWO economics. This was noticed from obtaining higher destruction in the presence of IPA at the same operating temperature. Thus, the removal of 99.22% (w/ IPA @ 525^{o}C) as a good value was obtained at a temperature lower than the actual needed in the absence of IPA. Using IPA as a co-fuel is a good option due to its rapid oxidation and generating free radicals.

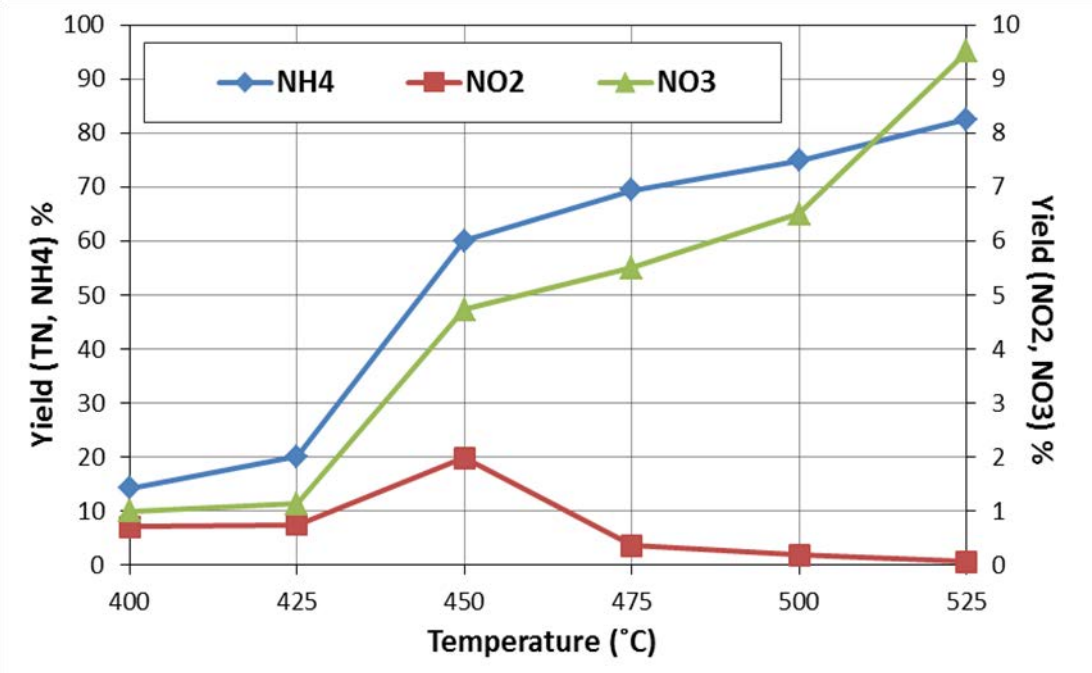


Figure 15: Nitrogen-Speciation yields as a function of temperature at 10 mM DMF, 1IPA/DMF ratio, SR of 1, 250 bar and 6 s.

Figure 15 above shows the yields of nitrogenous species in liquid phase as temperature increased in the presence of IPA and at 6 s residence time. It shows that increasing the temperature up to 525^{o}C was favoured for ammonia generation and thus this range of conditions is ideal for utilizing ammonia for useful applications. However, the sharp increase of ammonia in the presence of IPA indicates that adding co-fuel (IPA) would help to minimise the severe temperature normally needed for complete ammonia removal, where temperatures in excess of

650^{o}C would be required to completely decompose ammonia (Webley et al., 1991). Also, longer residence times can be another option. In other words, the decline point of ammonia is probably going to be at lower temperatures due to excess heat given by IPA in addition to generating more free radicals and the rapid oxidation of co-fuel. Nitrite (NO_2^-) was at its minimum values especially at temperatures from 500^{o}C onward, which indicated that nitrite decomposed further to Nitrate (NO_3^-) which is the most oxidative form of nitrogenous species in the liquid phase. Nitrate yield was increased with temperature and reached its max yield of 9.5% at 525^{o}C, which corresponds to 53 mg/l, where higher temperatures are needed for better removal. Higher temperature than those needed for ammonia are required to effectively decrease nitrate and nitrite (Cabeza et al., 2011).

Nitrogen analysis showed a reduction in TN values in the feed from 839 mg/L to 133 mg/L at 525^{o}C, which indicates that the presence of IPA helped to convert DMF further to ammonia and thus to nitrogen gas (N_2).

Figure 16 shows a summary of the improvement in TOC removal, TN removal and ammonia yield at the same investigated temperatures and in the presence of IPA compared to non-IPA experiments taken from previous work in our department (Kings, 2012).

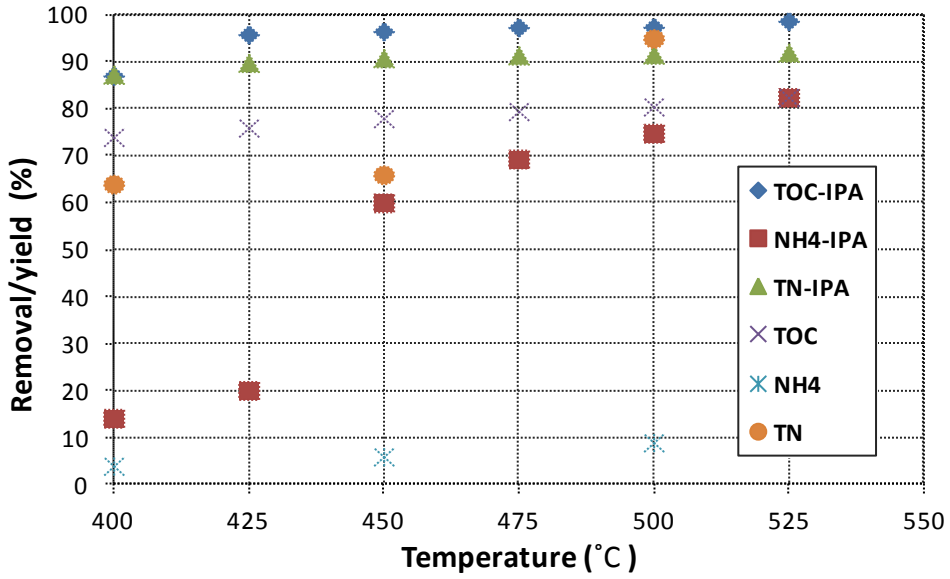


Figure 16: Effect of temperature on TOC, TN removals and NH_4 yield with and without IPA at 10 mM DMF, 1IPA/DMF ratio, SR of 1, 250 bar and 6 s.

First, it shows the improvement in TOC removal in the presence of IPA compared to non-IPA with an increase of 21% obtained at all temperatures investigated. Also, TN removal improved in a similar way with temperatures investigated in the presence of IPA. Moreover, it shows a dramatic increase in the yield of ammonia as the temperature increased when IPA was supplied. By coupling ammonia trend with high TN removal in figures 15 and 16, this showed that more conversion occurred for organic nitrogen (feed) and its major nitrogenous intermediates as TMA, DMA and MA towards ammonia and consequently to N_2, which is a sign of good destruction. Therefore, under investigated temperatures adding IPA enhanced the oxidation faster to form ammonia where a higher range of temperatures is needed to effectively eliminate ammonia that could not reach in this work due to oven capacity. In this work, this increase in the yield of ammonia during the investigated range of temperatures and in presence of IPA can be ideal for ammonia production if it is to be utilized for further applications as fertilizer industry.

4.4.4 Effect of DMF Concentration

The effect of initial DMF concentration on the SCWO of DMF was conducted at 400^{o}C, SR of 1, 1 IPA/DMF ratio, 250 bar and at a residence time from 2 to 10 seconds. The selected DMF feed concentrations were 1 mM, 5 mM, 10 mM, 15 mM and 20 mM at reactor entry (SC conditions). At ambient conditions, this range represents form 0.043 to 0.876 wt% and with the presence of IPA the maximum concentration reached in all experiments was 1.6 wt%. This is similar to the range that can be found in dilute wastewaters and also suits SCWO process that able to treat up to 20 wt% of aqueous waste (Brunner, 2009a). Also, to obtain controllable HPLC pump flow rates based on organic concentration selected, corresponding oxidant amount and the temperature. In addition, this range of DMF feed concentrations was selected to avoid any precipitation or excess heat affecting isothermal state of the lab-scale system used in this work.

Other conditions were kept at their minimal values during investigating DMF feed concentration to avoid effects overlap. IPA was fixed at 10 mM during investigating DMF concentrations which is the stoichiometric amount needed. The temperature of 400^{o}C was selected since organic concentration could be influenced by the dramatic change in the solution density at higher temperatures.

The results of DMF feed concentration effect were presented in form of TOC removal, TN removal and yields of Nitrogen-speciation in the presence of IPA compared to non-IPA system.

Figure 17 obviously shows the positive role of increasing DMF concentration on the TOC removal.

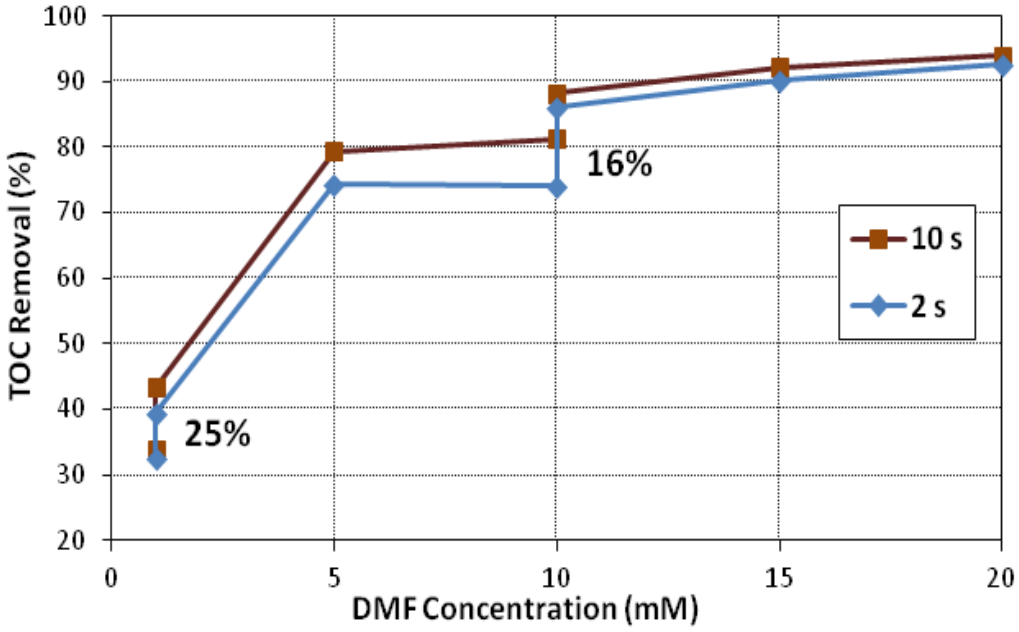


Figure 17: Effect of initial DMF concentration on TOC removal at 400°C, SR of 1, 1 IPA/DMF ratio, 250 bar and residence times of 2 and 10 s.

For examples, from a minimum TOC removal of 43.3% that obtained with 1 mM DMF, 10 s a considerable increase in the TOC removal of up to 117% was achieved at 20 mM DMF, 10 s where the maximum TOC removal reached at this point was 94%. Ding and co-workers observed a similar trend of increased TOC removal when organic feed concentration was increased (Ding et al., 1998). Also, in a similar work (without IPA) it was found that the TOC removal increased with DMF feed concentration (Pinto, 2004). There was an improvement in TOC removal with all DMF concentrations investigated, however increasing the DMF concentration by five-fold (like from 1mM to 5mM) showed a maximum increase of 85% over the studied range.

It is worth mentioning that all this improvement achieved in this part with DMF effect was obtained at a low temperature of 400°C, 1SR and only needed amount of IPA (IPA/DMF ratio of 1) based on reaction stoichiometry. Thus, higher or oven complete TOC removal is expected with slightly elevating some or all other conditions such as using higher IPA ratios, higher

temperatures and/or more oxidant at the same organic concentrations investigated. It was noticeable that increasing DMF concentration up to 20 mM was still driving the destruction forward as more organic provides extra enthalpy and thus enhances generated heat (Cabeza et al., 2011). Thus, it is expected that above 20 mM of DMF would achieve a significant conversion with only 400^{o}C applied in this part of the work. However, obtaining uncontrollable flowrates disallowed to use higher DMF concentrations.

Figure 17 also shows clearly how adding IPA enhanced the TOC removal and subsequent DMF oxidation. For example, there was a significant improvement in TOC removal by around 25% when 1 mM IPA was added to 1 mM DMF at similar conditions (400^{o}C, SR of 1). Also, with 10 mM of DMF the presence 10 mM IPA clearly improved the TOC removal by 16% compared to the same experiment without IPA.

The enhancement in the removal made by adding IPA also can be seen in figure 18 by looking to the difference between round dotted lines (no IPA) and their corresponding solid lines. Both Figures (17 & 18) showed that the TOC removal from oxidizing 10 mM DMF without IPA was almost equivalent the effect of 5 mM DMF when IPA added. This shows that adding even just stoichiometric amount of IPA would double the effect of the organic material (DMF) at any feed concentration.

Figure 18 also shows that the studied range of residence time has a minor positive influence on the SCWO of DMF during investigating initial DMF concentration. For example, the figure shows clearly that no big difference even between 10 s and 2 s. Also, noticed that the effect of residence time becomes slightly less as DMF increased since DMF effect become more dominant. It can be concluded that there would be no further enhancement by using longer residence time (bigger reactor) within the range of conditions studied in this part, where the focus should be on other conditions.

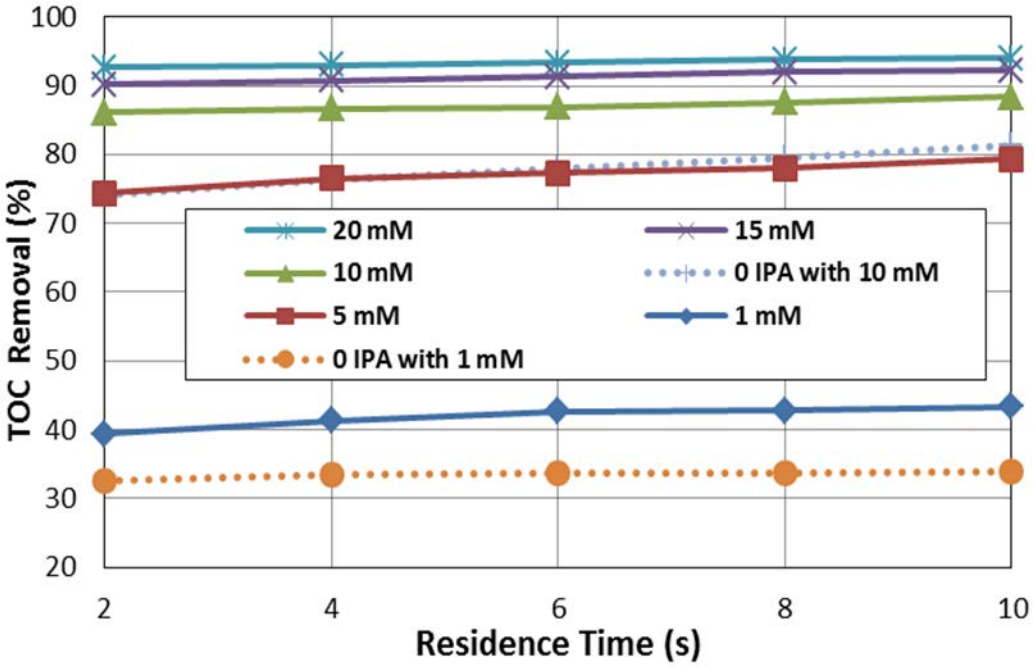


Figure 18: TOC removal against residence time at varying initial DMF concentrations and at 400 ^{o}C, SR of 1, 1 IPA/DMF ratio and 250 bar.

Figure 19 displays the yield of nitrogen-species in the liquid phase with DMF feed concentration in the presence of IPA at 6 s of residence time. It clearly shows that increasing DMF feed concentration from 1 to 20 mM increased the yield of ammonia, nitrite and nitrate in the liquid phase. Also, using up to 20 mM of DMF was still shifting the reaction to produce more nitrogen-species as more organic enhances radical generation and therefore the conversion.

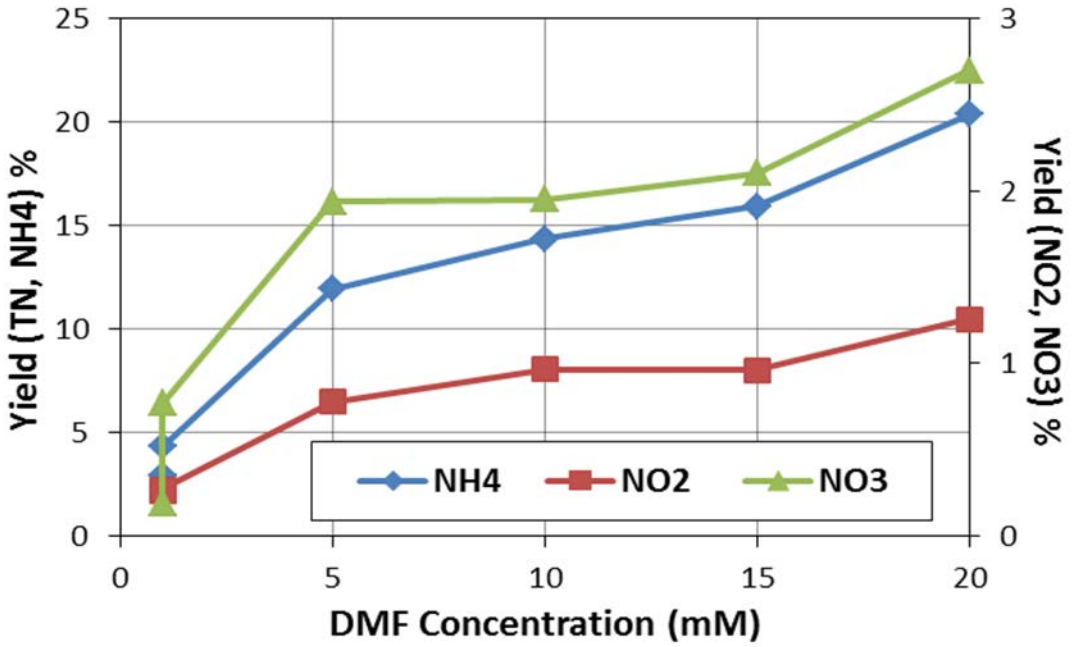


Figure 19: Nitrogen-Speciation yields as a function of DMF concentration at 400°C, 1IPA/DMF ratio, SR of 1, 250 bar and 6 s.

The graph shows an increase in the yield of ammonia with DMF feed concentration and was still low to show any potential to significantly decline due to using low temperature of 400°C. This matches another work that showed at lower temperature of 400°C, the yield of ammonia increased with DMF feed concentration, while the trend inverted at higher temperatures and also with more oxidant (Pinto, 2004). Also, there was a slight increase in the yield of nitrite (NO_2^-) and nitrate (NO_3^-) with DMF feed concentration, but they were at low values due to the lower temperature used, 400°C. Therefore, using higher temperatures is necessary to make further destruction for nitrite and nitrate.

Comparing the baseline experiment that was carried at (1mM DMF, 0 IPA, 400°C, 1 SR) to its corresponding experiment when 1 mM IPA added, showed that the addition of IPA slightly increased the yield of ammonia, which is probably due to lower temperature used. Also, the yield of nitrite and nitrate showed a slight increase with IPA. A similar trend for nitrate and nitrite was

observed with another co-fuel (methanol), in which their concentrations increased in the liquid effluent (Oe et al., 2007). This observation was also noticed with ammonia in previous temperature set, where using more IPA, more oxidant ratios and/or even using slightly higher temperatures could force ammonia to be reduced. In conclusion, adding stoichiometric IPA in this part did not help to reduce ammonia due to using minimum values of operating conditions, where elevating them would help to find optimum conditions to effectively reduce ammonia as an intermediate.

Figure 20 shows a broader picture for TOC and TN removals and the yield of ammonia. First, it shows the similarity in the improvement of TOC and TN removal with DMF feed concentration in the presence of IPA compared to non-IPA experiments. This increase in both removals is due to that more organic (DMF) leads to more radicals and thus a better conversion achieved. The similarity in both removals is due to carbon and nitrogen forming the backbone of organic material.

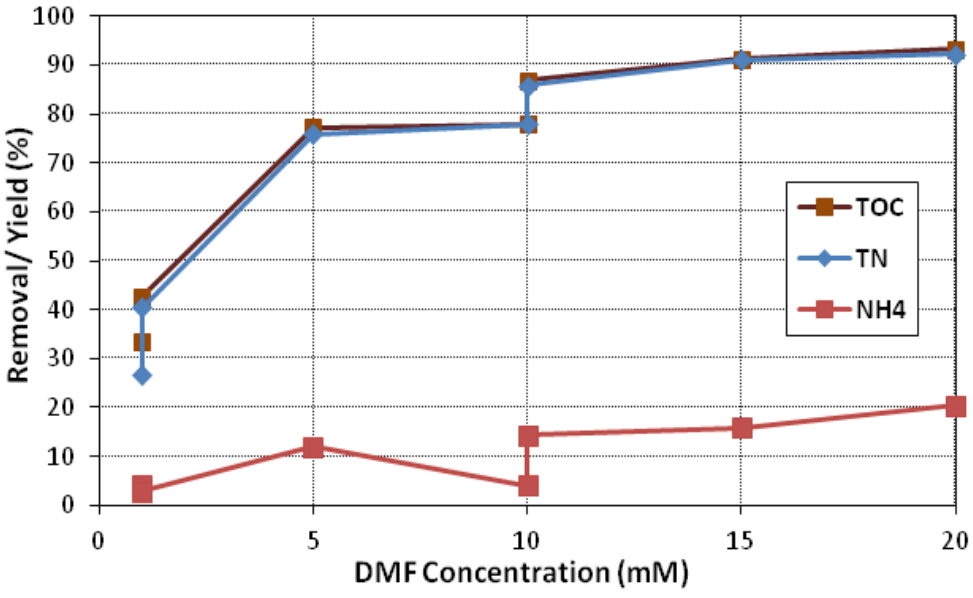


Figure 20: Effect of DMF feed concentration on TOC, TN removals and NH4 yield with and without IPA at 400^{o}C , 1IPA/DMF ratio, SR of 1, 250 bar and 6 s.

The significant effect of adding IPA on TOC and TN removal improvement can be seen by referring to the two baseline experiments that were conducted at 1mM and 10 mM DMF in the absence of IPA. For example, with 10 mM of DMF and in the presence of IPA the TOC and TN removals improved by 11% at 6 s of residence time. This improvement occurred though only a stoichiometric amount of IPA (IPA/DMF ratio =1) was used during DMF feed concentration investigation and at 400^{o}C, in which this can be attributed to the extra enthalpy value and free radicals produced in the presence of IPA. Interestingly, it was noticed that effect of 10 mM DMF without IPA has a similar effect as that of 5 mM DMF in the presence of IPA indicating that IPA added an effect equivalent to the effect that can be obtained by doubling the organic material concentration, however adding IPA is more convenient due to radical production. Also, there was an increase in the yield of ammonia when IPA (10 mM IPA) added with 10 mM DMF as seen in figure 19. Thus, it can be concluded that using higher IPA ratios, more of oxidant and/or longer residence time or even relatively higher temperatures are needed to significantly reduce ammonia as an intermediate, especially that IPA obviously helped to enhance the TOC and TN conversions further.

4.4.5 Effect of Oxidant Ratio

The reactions equations for complete oxidation of dimethylformamide (DMF) in the absence and presence of IPA are shown in equations 4.1 and 4.2 in Section 4.2.

Supplying enough oxidant is necessary during treating organic in hydrothermal environment as in the case of SCWO of DMF and IPA in order to initiate oxidation reaction. Thus, the role of oxidant ratio on DMF and IPA oxidation was tested at various ratios from 0.8 SR to 2 SR, which represents 80% of needed oxidant for complete oxidation to two times higher than the needed

amount (100% excess oxidant). The selected range of oxidant ratios was also based on the controllable HPLC pump flow rates according to organic concentration selected, corresponding oxidant amount and the temperature. Also, this range is to cover a specific area of oxidant ratios as more oxidant is not favourable for large scale application due to cost and control challenges. Other conditions were kept at a temperature of 400°C, initial DMF concentration of 10 mM, 1 IPA/DMF ratio and 250 bar.

The results of oxidant ratio effect were presented in forms of TOC removal, TN removal and yield of Nitrogen-speciation where also all figures were presented to show the enhancement in oxidant role in the presence of IPA compared to non-IPA system.

Figure 21 illustrates the effect of different oxidant ratios on TOC removal at various residence times (2-10 s) and in the presence of IPA.

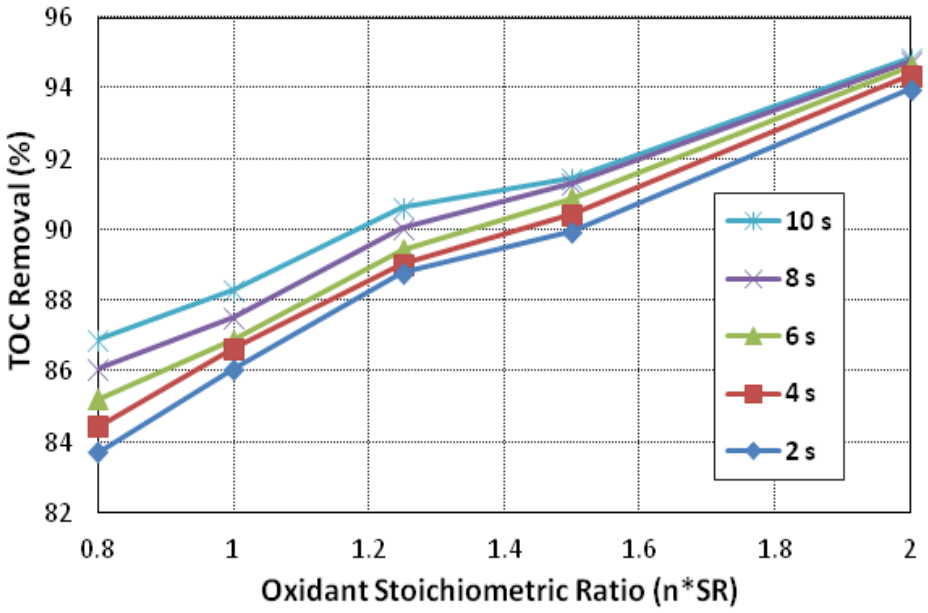


Figure 21: Effect of oxidant stoichiometric ratio on TOC removal at 400°C, 10 mM DMF, 1 IPA/DMF ratio, 250 bar and various residence times.

This graph clearly shows the positive dependence of TOC removal on oxidant as the ratio ranged from deficit (0.8 SR) to 100% excess (2 SR). This is in agreement with other studies that

found increasing oxygen positively affected the TOC conversion (Cocero et al., 2000a, Cabeza et al., 2014). Also, the trend of enhancement made by oxidant ratios partly disagrees with another study that reported that oxidant has no much further effect above 1.2 SR (Cocero et al., 2000a). In a similar work on DMF, it was found that with a 60% excess of oxygen, complete TOC removal was achieved at 500^{o}C and at 6.6 seconds residence time (Pinto, 2004). This is probably since in this work adding IPA gave more effect for the oxidation by generating more free radicals. A minimum TOC removal of 87% was obtained with 0.8 SR after 10 s, which is due to using 20% deficit oxidant, while the maximum TOC removal was 94.9% with 2 SR after 10 s. Also, here the trend shows that above 2 SR more destruction is expected. This maximum removal by doubling oxidant amount is close to that was obtained with DMF concentration effect, 93.99%, when DMF concentration was 20 mM.

Figure 22 shows more the effects of residence time, hydrolysis and the enhancement made by IPA when added compared to one non-IPA experiment. First, it shows how adding IPA (solid brown line) enhanced DMF destruction compared to the same experiment without IPA (blue round dot line) at same other conditions (400^{o}C, 10 mM DMF and 1 SR) where the improvement in TOC removal was around 16.3% and 9% at 2 s and 10 s, respectively.

Also, it shows how residence time positively affected the TOC removal at all oxidant ratios investigated. However, its effect on TOC removal was marginal as it increased from 2 s to 10s especially in presence of IPA experiments. For example, for 1 SR experiment (in the presence of IPA) the TOC removal improved only by around 2.6% when residence time increased from 2 s to 10s, and also by similar percentage (2%) with 1.25 SR experiment (in the presence of IPA) when residence time increased by the same range. This proves that not much further destruction is expected from using a longer reaction time in order to improve the efficiency of SCWO process. It was noticed that residence time becomes less effective at higher oxidant ratios as oxidant

becomes dominant over all other variables, this also can be seen in Figure 21. For example, with 0.8 SR the TOC removal enhanced by 3.8% when residence time increased from 2 s to 10 s, and with 2 SR it increased by 1% at the same residence time range. It is worth mentioning that all oxidant effect experiments were conducted at lower temperature as 400^{o}C, 10 mM DMF and 1 IPA/DMF ratio, in which with relatively higher conditions or more oxidant a better or even full TOC removal can be achieved.

Figure 22 shows also the minor effect of hydrolysis (orange square dotted line) on DMF decomposition that was in the absence of oxidant at the same conditions (400^{o}C, 10 mM DMF, 1 IPA/DMF ratio). Results showed around 5.2% of TOC removal was obtained after 10 seconds of residence time, which completely agrees with other work. For instance, Pinto showed that DMF could be thermally destroyed in the absence of oxygen, where the TOC removal was 6±4.3% at 6 seconds and a temperature of 600^{o}C (Pinto, 2004). Also, others showed that the minor role of hydrolysis for organics in the preheater can reach up to 4% (Segond et al., 2002, Ploeger et al., 2007). These results indicate that hydrolysis is expected to occur for the organic matter in the preheater, but it would represent a small portion of the destruction where most of the effect comes from oxidant when presents in hydrothermal process. This is due to the fact that oxygen participates effectively in free radical generation that enhances oxidation reactions.

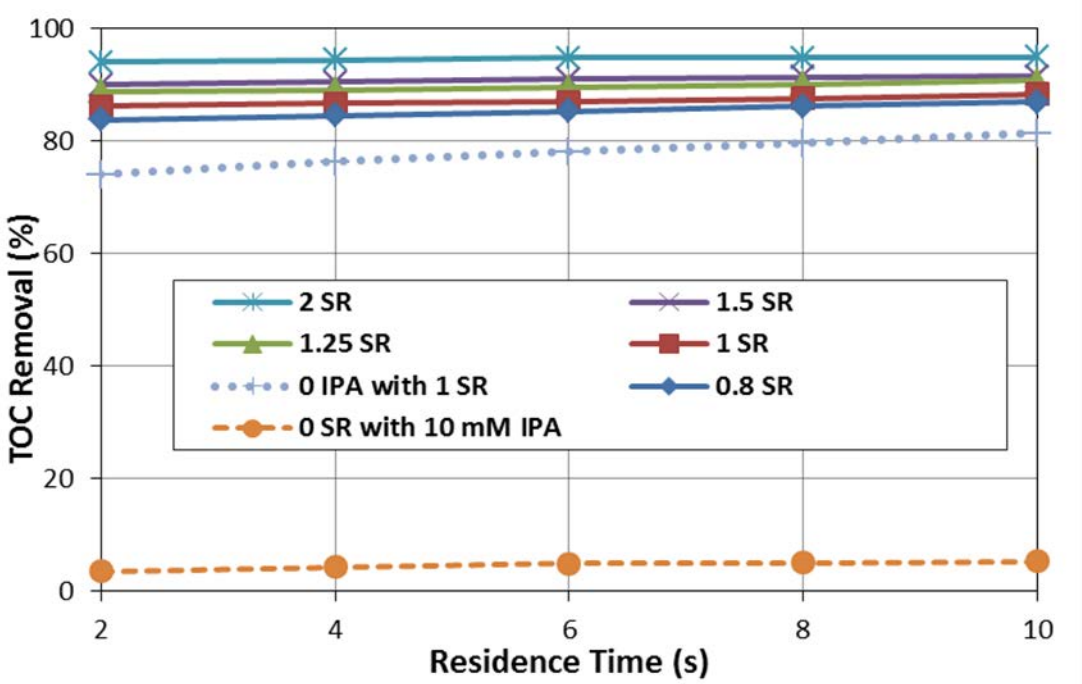


Figure 22: TOC removal against residence time at varying oxidant stoichiometric ratios and at 400^{o}C, 10 mM DMF, 1 IPA/DMF ratio, 0 IPA and 250 bar.

Figure 23 displays the yield of nitrogen-speciation in the liquid phase with varying ratios of oxidant and in the presence of IPA at 6 s of reaction time. First, it shows the very low yield of ammonia, nitrite and nitrate during hydrolysis reaction indicating the importance of oxidant to convert DMF to its final nitrogen-products. Secondly, as oxidant increased from a sub-stoichiometric level to a 100% excess (2 SR), there was an increase in the yield of ammonia. Nitrite and nitrate fluctuated as oxidant increased, where higher temperatures are needed for their conversion to N_2. Generally, it has been found that increasing oxygen level decreased ammonia yield, while nitrate and nitrite concentrations increased during organic oxidation (Killilea et al., 1992, Oe et al., 2007, Cabeza et al., 2011). A similar observation was reported during DMF oxidation as oxygen increased at 500^{o}C and at 6.6 seconds (Pinto, 2004). Accordingly, it was recommended by several authors to use 1 SR in order to improve ammonia yield and minimise the levels of nitrate and nitrite (Cocero et al., 2000a, Oe et al., 2007). This range of oxidant till 2

SR did not reduce ammonia yield as unwanted by-product due to using lower temperature of 400°C during investigating oxidant effect even with IPA presence. Therefore, using more IPA with relatively higher temperatures and with the same range of oxidant is expected to reduce the yield of ammonia and other species into N_2. It seems that the conditions used in this part are still suitable for ammonia production even IPA helped to shift the TOC and TN conversions further. The observed reduction in all nitro-species as oxidant ratio ranged from 0.8 to 1.25 supports the suggestion that using 1SR is favourable to decrease their yields.

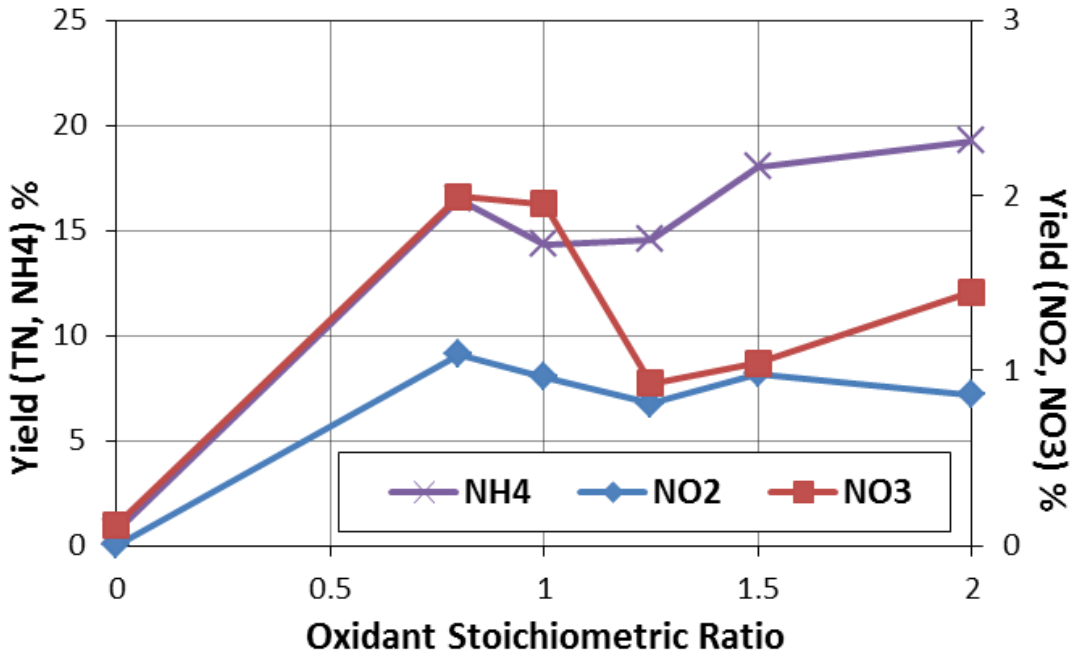


Figure 23: Nitrogen-Speciation yields as a function of oxidant stoichiometric ratio at 400°C, 10 mM DMF, 1IPA/DMF ratio, 250 bar and 6 s.

A broader picture for TOC and TN removals in addition to the yield of ammonia are shown in Figure 24. First, it shows clearly the very low removals of TOC and TN during hydrolysis reaction in addition to the poor effect on the yield of ammonia. However, hydrolysis affected TOC removal, 5%, more than TN removal that was at minimal value (almost zero removal), which is due to the complex chemistry of organic nitrogen compared to the organic carbon.

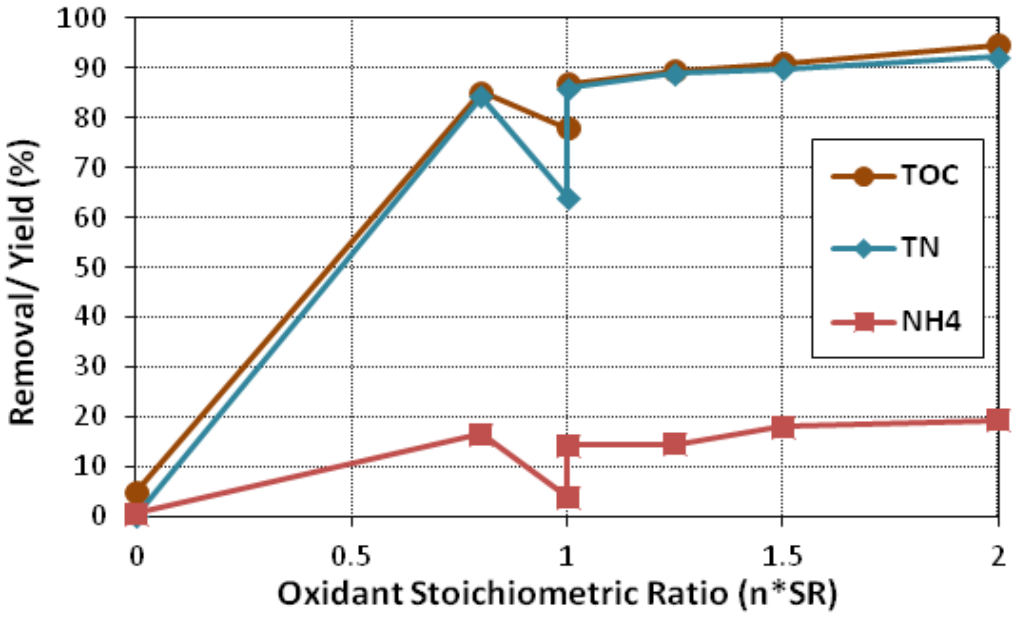


Figure 24: Effect of oxidant stoichiometric ratio on TOC, TN removals and ammonia yield with and without IPA at 400^{o}C, 1IPA/DMF ratio, 250 bar and 6 s.

Secondly, increasing oxidant ratio from 0.8 SR to 2 SR (w/ IPA) clearly enhanced the removals of TOC and TN in addition to increasing the yield of ammonia. Also, the graph shows how adding IPA significantly enhanced both TOC and TN removal to 86% compared to non-IPA experiment (at 1SR) where their values were 78% and 64% respectively. Also, the yield of ammonia increased more than twofold. This increase in the yield of ammonia eventually would allow for the possibility to decrease ammonia production at lower temperatures than the typically needed especially when higher IPA ratios are used. The presence of co-fuel enhanced the oxidation via enhancing free radical generation in addition to excess heat produced due to high calorific value of IPA. Lastly, there is a similarity in the trends of TOC and TN conversions with varying oxidant ratios as both carbon and nitrogen form the backbone of DMF.

4.4.6 Effect of IPA Concentration Ratio

Studying the effect of varying ratios of IPA/DMF concentrations is necessary in order to evaluate the role of IPA on DMF treatability by SCWO. Thus, the effect of different IPA concentration ratios on the SCWO of DMF was conducted at 400°C, 1 SR, 10 mM DMF, 250 bar and at residence times from 2 s to 10 s. The IPA concentration ratios investigated were 1 mM, 5 mM, 10 mM, 15 mM, 20 mM and 30 mM that represent IPA/DMF ratios of 0.1, 0.5, 1, 1.5, 2 and 3. These ratios were selected to obtain controllable HPLC pump flow rates based on organic (DMF and IPA) concentrations, corresponding oxidant amount and the temperature. Also, in order to avoid any excess heat affecting isothermal state of the reactor. All other conditions were kept at their minimal values during IPA ratio effect tests to avoid overlap with other conditions. The results of IPA effect were presented in the form of TOC removal, TN removal and yield of Nitrogen-speciation. Figure 25 illustrates the effect of varying IPA ratios on TOC removal at various residence times (2-10 s).

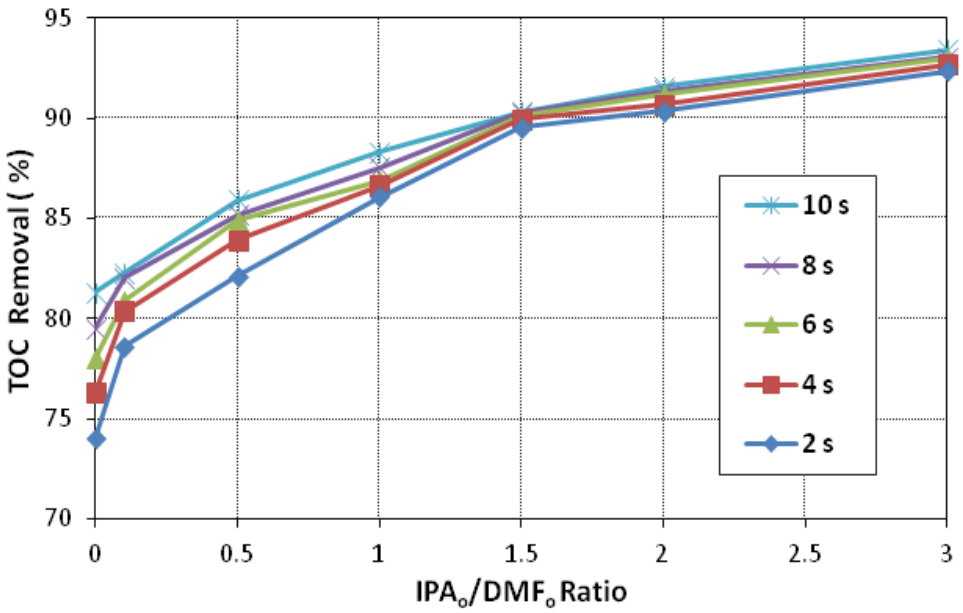


Figure 25: Effect of IPA/DMF ratio on TOC removal at 400°C, 10 mM DMF, 1 SR, 250 bar and various residence times.

First, the figure shows how the presence of IPA positively affected the TOC removal compared to non-IPA baseline experiment (zero IPA), where for instance with IPA/DMF ratio of 1, the TOC removal improved by around 9% compared to IPA-free experiment. Secondly, adding IPA significantly improved the TOC removal and thus DMF destruction over the studied ratios of IPA/DMF (from 0.1 to 3 ratios). For example, the TOC removal improved from 82.3% when IPA/DMF ratio was 0.1 to 93.4% at the ratio of 3 and at a residence time of 10 s. Also, there is still a gap to be filled above IPA ratio of 3. Previous works found that using co-fuels such as ethanol and methanol positively increased TOC and organic matter destruction (Ploeger et al., 2006a, Ploeger et al., 2007). Generally, IPA as a co-fuel is more efficient than such co-fuels and thus it would be reasonable to be more efficient. The positive role of IPA was due to its high calorific value where high temperatures are produced via exothermic reaction and thus a better destruction obtained (Bermejo et al., 2008, Cabeza et al., 2011).

In addition, the graph shows the positive effect of residence time on the TOC removal especially at lower IPA ratios, where the effect of IPA dominates with higher IPA ratios. However, the closure and minor improvement in the TOC removal with residence time indicates that there is no necessity to use longer reactors (higher residence time) in order to improve the destruction in which other variables must be deeply investigated and optimised. Finally, although temperature is the most influential variable, it is clear from IPA effect that higher IPA ratios would enhance the destruction further, where IPA is cheaper way than using costly external heat source.

Figure 26 displays the yield of nitrogen-speciation in the liquid phase with varying IPA ratios at 6 s of residence time. The presence of IPA did not clearly reduce the yield of ammonia as there was a fluctuation with all IPA ratios investigated. The fluctuation in the yield of ammonia was probably due to the lower temperature (400^{o}C) used in this work, in which more

IPA or even associated with higher temperatures would ultimately reduce its yield. An analytical error was also expected due to the sensitive procedure of ammonia analysis.

On the other hand, the yield of nitrite (NO_2^-) clearly decreased with all IPA ratios to reach its minimal level at an IPA ratio of 3. Nitrate (NO_3^-) showed no clear trend, which is probably due to an analytical error occurred at that point.

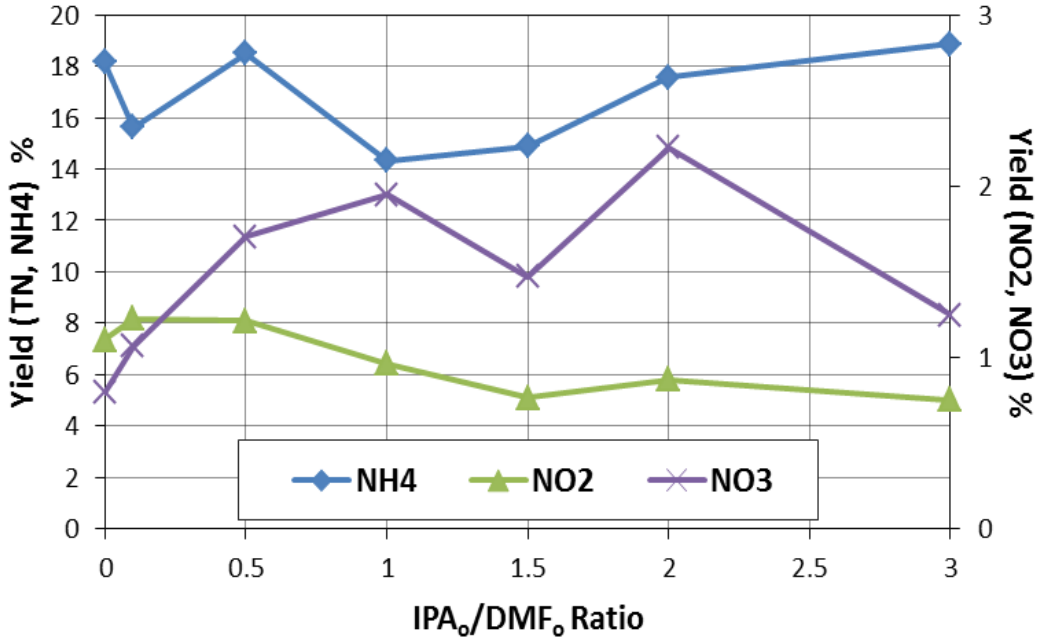


Figure 26: Nitrogen-Speciation yields as a function of IPA/DMF ratio at 400°C, 10 mM DMF, 1 SR, 250 bar and 6 s.

A broader picture for the TOC and TN removal in addition to the yield of ammonia can be seen as in Figure 27 after 6 s of residence time. It shows how adding IPA (even with an IPA ratio of 0.1) improved both removals compared to in the absence of IPA. Then, the TOC and TN removals showed a continuous and similar increase with all IPA/DMF ratios used indicating higher IPA ratios would improve the DMF destruction further. The similarity in both removals is due to that carbon and nitrogen represent the backbone of organic material. The slight deviation in TN removal is due to the fact that nitrogen is more refractory than carbon. In case of ammonia,

its yield fluctuated with all IPA ratios used, which was probably due to using low temperature of 400°C, 1 SR or even due an analytical error. The positive effect of IPA on TOC and TN removals ultimately seems reasonable to enhance the reduction of ammonia yield as unwanted intermediate and that more nitrogen in the liquid effluent converted to nitrogen gas.

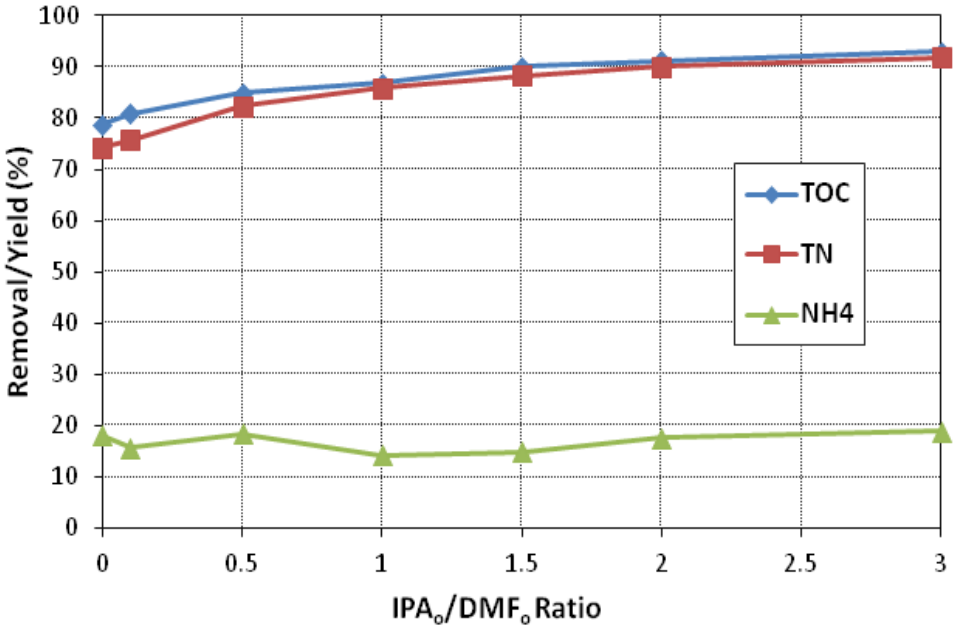


Figure 27: Effect IPA/DMF ratio on TOC, TN removals and NH4 yield at 400°C, 10 mM DMF, 1 SR, 250 bar and 6 s.

4.5 Summary

Temperature was the most influential variable on DMF destruction as the maximum TOC removal was 99.22% at 525°C, which indicates a complete DMF removal could be achieved at the same temperature as DMF conversion always ≥ TOC removal or even by slightly elevating other conditions. DMF feed concentration and oxidant ratio affected TOC removal positively as they increased, but with less extent than that of temperatures. The presence of IPA as a co-fuel either during investigating previous variables or when studied alone clearly enhanced the TOC removal even low temperature of 400°C was used when each independent variable investigated.

Thus, the destruction of DMF was significantly enhanced where not many studies have been conducted on treating nitrogenous-aliphatic compounds with co-fuels except ammonia. Also, the TN removal improved with all investigated variables in a similar manner as that of TOC removal.

There was an increase in the yield of ammonia when investigating the effects of temperature, DMF feed concentration and oxidant even in the presence of IPA. This was due to using only the stoichiometric IPA and also due to using lower temperature range (400-525^{o}C). During investigating IPA effect, ammonia fluctuated with all IPA ratios, which is due to the lower temperature (400^{o}C) used with this set. Combing TN removal that enhanced in the presence of IPA indicates that ammonia can be reduced with more IPA dosage and probably higher temperatures.

Hydrolysis experiments proved that no significant hydrothermal decomposition occurred for DMF inside the preheater as only a maximum removal of 10% was achieved where most of destruction occurs only when oxidant was supplied.

It was observed a considerable destruction at the early stages of the reaction (during first 2 s), which was due to the relatively high temperatures of oxidation reaction in SCWO, and also due to the good mixing (high solubility) of organic and oxidant streams at reactor entry that enhances reactant contact and thus free radical production.

According to TOC results, it was obvious that the addition of co-fuel decreased the necessary operating temperatures in possibly a cheaper way than consuming more external heat. Therefore, this would help to eliminate ammonia at lower operating temperatures than normally needed. The positive effect of IPA on the destruction was due to generating excess heat and free radicals in addition to its rapid oxidation. Recovering excess heat in addition to lowering needed system temperature would effectively improve the process economics in the future.

4.6 Global Kinetics of DMF Oxidation

In the absence of detailed reaction mechanisms, quantifying the global reaction rate by identifying the main SCWO pathways is sufficient for engineering design purpose. Type and amount of formed intermediates during early stages of oxidation reaction also govern the reaction rate in addition to main role of starting organic material. Usually in all the SCWO of nitrogen-containing compounds ammonia is the main and most refractory intermediate. Moreover, reaction mechanism could be influenced by the oxidant.

The qualitative investigation of the effects of different process variables as temperature, organic concentration, oxidant ratio and residence time on DMF decomposition kinetics was performed as previously illustrated in Section 4.4.

To study quantitatively the effects of these parameters, the kinetic analysis was conducted to find reaction rate parameters as reaction rate constant (*K*), Arrhenius parameters (activation energy and pre-exponential factor) and the orders of reaction with respect to DMF (a), oxidant (b) and water (c) using global power-rate law expression. Most of SCWO kinetic models have been developed from the global rate law expression as in equation (4.4) below:

$$\frac{-d[Organic]}{dt} = k[organic]^a[oxidant]^b[H_2O]^c = A\exp^{\left(-\frac{Ea}{RT}\right)}[organic]^a[oxidant]^b[H_2O]^c \quad (4.4)$$

Where

k= Reaction rate constant in $M^{1-a-b-c}\ s^{-1}$

[organic] = organic compound initial concentration (mol/L) at reactor entry

[oxidant]= oxidant initial concentration (mol/L) at reactor entry

A = Pre-exponential factor in $M^{1-a-b-c}\ s^{-1}$

E_a = activation energy in J/mol

R = Universal gas constant (8.314 J/mol.K)

T = Reaction temperature (K)

a = Reaction order with respect to the reactant organic compound

b= Reaction order with respect to the oxidant

c= Reaction order with respect to the water

Several SCWO kinetic studies have been carried out (as explained in literature survey) either on waste mixtures or on single compounds under different conditions of temperatures, residence times, organic concentrations and with using different reactor designs. The studies then presented kinetic parameters and the global rate-law expressions.

In this study, the obtained experimental data were used to describe the DMF oxidation kinetics, in which the approximation of global rate-law expression for DMF was done using these methods:

- Pseudo –first-order approximation

- Integral method approximation

Water as a reaction medium for the SCWO of DMF represents more than 99% of water (in excess), therefore the concentration of water was considered constant that has no effect on the DMF oxidation rate. Thus, reaction order with respect to water is zero.

4.6.1 Pseudo-First-Order Approximation

The global kinetics for SCWO of organic wastewaters have been described by several researchers by pseudo-first-order expression, that expresses a reaction of order of one with respect to the organic and zero with respect to oxygen (Helling and Tester, 1988, Pinto et al., 2006b, Abelleira et al., 2013). This is a good initial simplification as the oxygen used in all runs was always in excess to ensure complete oxidation of DMF. This makes the global power-rate law expression as follows:

$$rate = \frac{-d[DMF]}{dt} = k[DMF] \quad (4.5)$$

And since TOC values are the main experimental conversion data from DMF oxidation, the equation was modified to be:

$$rate = \frac{-d[TOC_{DMF}]}{dt} = k[TOC_{DMF}] \quad (4.6)$$

By integrating equation 4.6, the following equation can be plotted:

$$ln\left(\frac{[TOC]}{[TOCo]}\right) = -k.t \quad (4.7)$$

Then, natural logarithm of TOC concentration at reactor exist divided by initial TOC content versus residence time was plotted for each temperature investigated as illustrated in Figure 28. Then, the rate constant (*k*) for each temperature was obtained from the slope of each linear fit as shown Table 12.

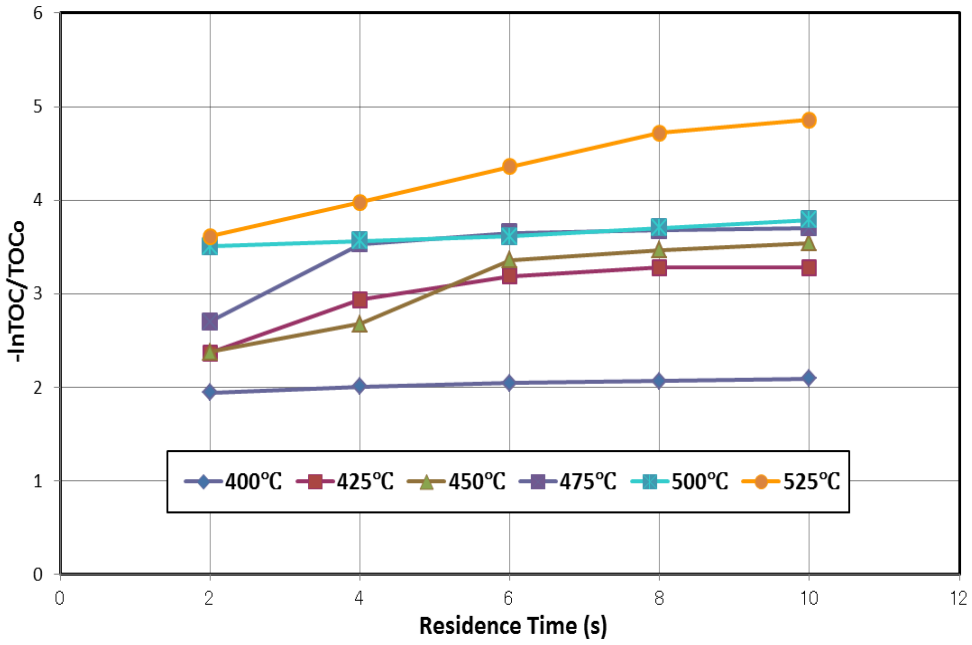


Figure 28: Natural logarithm of (TOC/TOC_O) versus residence time for DMF experiments at studied temperatures and a pressure of 250 bar.

Table 12: Rate constants for all temperature experiments.

Temperature (K)	Residence time (s)	Rate constant, k (s^{-1})
673.15	2-10	0.0177
698.15	2-10	0.1083
723.15	2-10	0.1536
748.15	2-10	0.1076
773.15	2-10	0.0353
798.15	2-10	0.1614

In order to determine Arrhenius parameters as activation energy (*Ea*) and pre-exponential factor (*A*), the natural logarithm of the obtained rate constant (*k*) for each temperature plotted versus temperature inverse (1/T) as shown in Figure 29.

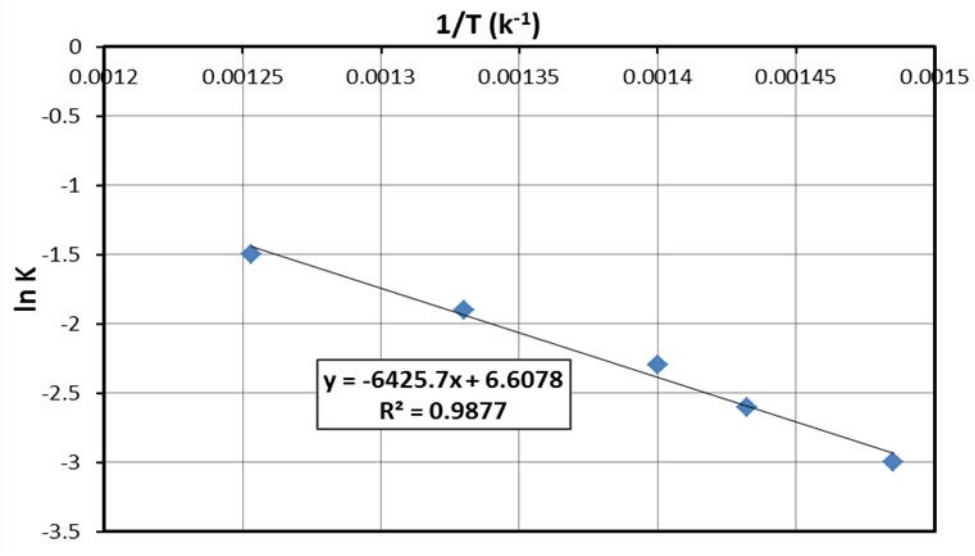


Figure 29: Arrhenius plot for the oxidation of DMF.

Therefore, the value of activation energy was determined by multiplying the slop (i.e. 6425) by the universal gas constant (8.314 J/mol.K) that gave *E*a= 53423.3 J/mol and the value of pre-exponential factor was calculated from ln *A*= intercept, and this gave $A = 4.09 \times 10^4$ s^{-1}. Therefore, the emerged Pseudo-first-order rate expression for the oxidation of DMF (via TOC_{DMF}) at the temperatures investigated is given by:

$$\text{rate} = \frac{-\text{d}[\text{TOC}_{\text{DMF}}]}{\text{dt}} = 4.09 \times 10^4 \ (\text{s}^{-1}) \exp\left(-\frac{53423 \ \text{J/mol}}{\text{RT}}\right)[\text{TOC}_{\text{DMF}}] \qquad (4.8)$$

4.6.2 Integral method approximation

To understand more the development of the global rate expression for DMF oxidation, integral method approximation was used to mathematically express the kinetic data. To determine the global kinetic parameters for DMF oxidation equation (4.4) was used considering that the order of DMF equal to one. These parameters were regressed from the complete set of data to predict the reaction rate of DMF oxidation over the conditions investigated and by assuming that the destruction of DMF is only a function of temperature, DMF and oxygen concentrations as by water was always in excess amount (>99% water). Although some works of oxidation kinetics in SCWO suggested that the oxygen has a minor effect or an order of zero (as previously discussed), it is worth discovering any influence of oxygen concentration on the DMF destruction. Therefore, oxidant effect experiments were carried out at 400°C, 10 mM DMF concentration, 250 bars and with five oxidant ratios (from 0.8 SR to 2 SR) that represent from 70 mM to 175 mM oxidant concentration at reactor inlet. The TOC removal for these experiments was shown in Figure 21 in Section 4.4.5. It showed an obvious increase in the TOC removal as oxygen concentration increased. Thus, oxidant has an effect and the order of reaction with respect to oxygen should be higher than zero and then the previous assumption (Pseudo-first order approximation) for DMF destruction needs to be assessed. Therefore, PFR design equation was used to determine the order

of oxygen using integral method approximation with *a*=1 and *b*>zero where equation 4.4 can be rearranged as below:

$$(-\mathrm{rA}) = \frac{-d[DMF]}{dt} = k\,[DMF][O_2]^b = A\exp^{\left(-\frac{\mathrm{Ea}}{\mathrm{RT}}\right)}[DMF][\mathrm{O_2}]^b \qquad (4.9)$$

The concentration of oxidant can be assumed constant ($[O_2]=[O_2]_o$). The performance equation for steady-state plug flow reactor was applied (Levenspiel, 1999) as follows:

$$\frac{\tau}{[DMF]_O} = \int_0^X \frac{dX_{DMF}}{(-rA)} \qquad (4.10)$$

Where $\boldsymbol{\tau}$ is the residence time, [DMF]o is the DMF initial concentration, X_A is the conversion of DMF and ($-r_A$) is the reaction rate for the SCWO of DMF.

Substituting equation 4.9 into PFR performance equation yielded the following equation:

$$\ln\left(\frac{1}{(1-X_{DMF})}\right) = k.t[\mathrm{O_2}]_o^b \qquad (4.11)$$

Thus, to determine the numerical estimate of b value, it is essential to plot ln[1/(1-X)] versus $\boldsymbol{\tau}$ for oxygen concentration experiments. Then, the slopes of all straight lines produced $k[\mathrm{O_2}]_o^b$ as shown in Figure 30.

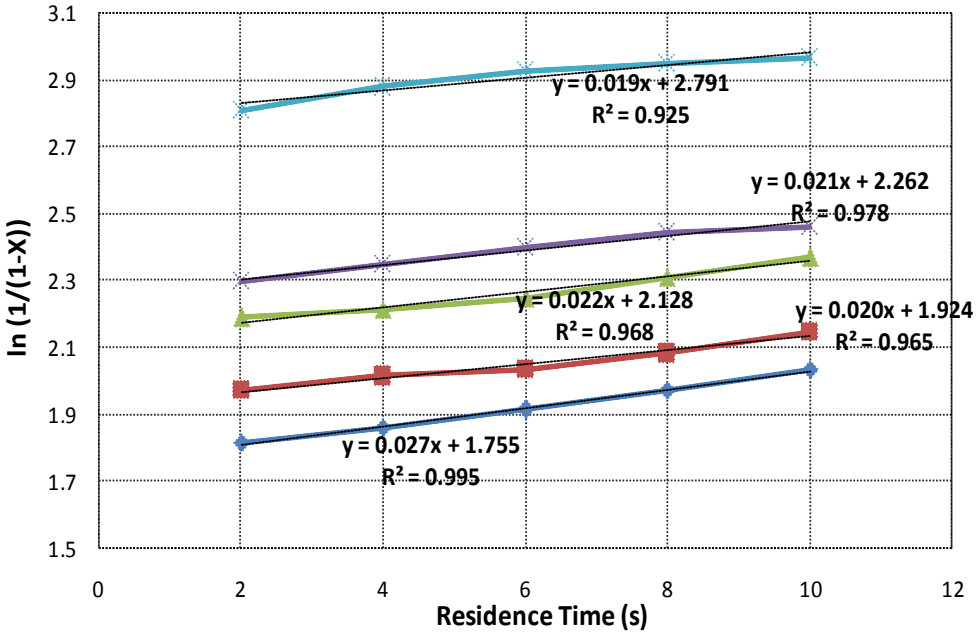


Figure 30: Natural logarithm of (1/(1-X)) versus residence time for DMF experiments with varying oxidant concentrations.

By taking the natural logarithm of $k[O_2]_o^b$, this term can be written as:

$$\ln (k[O_2]_o^b) = \ln (k) + b \ln ([O_2]_o) \quad (4.12)$$

Therefore, plotting these slopes ($k[O_2]_o^b$) from figure 30 as a function of the oxygen concentration on a logscale will produce a straight line with a gradient of b as shown in Figure 31.

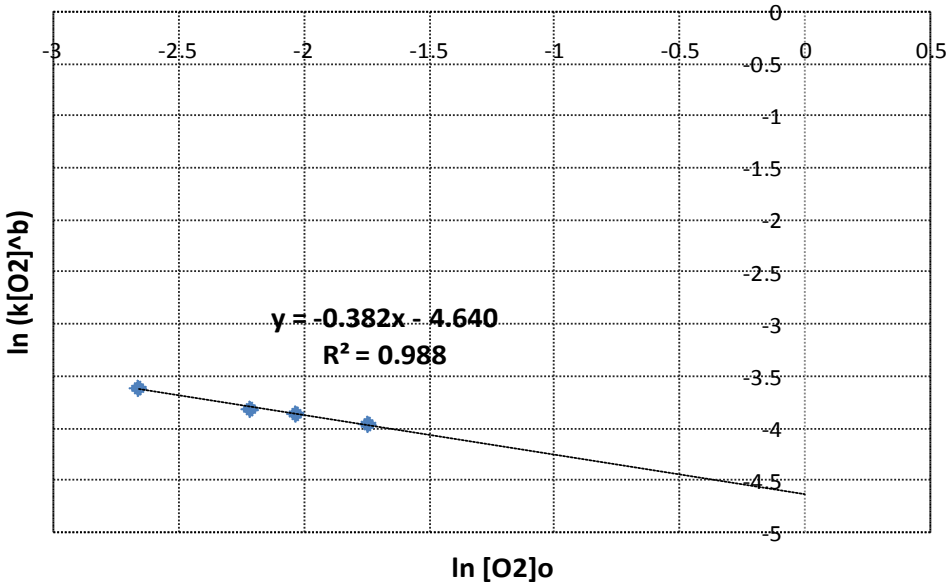


Figure 31: Determination of oxygen reaction order.

The slope of the straight line was 0.38 which is the order (*b*) of reaction with respect to oxygen. By determination of the reaction orders for the global rate law for DMF and oxygen as (*a*=1 and *b*=0.38), to determine the values of k previous equation (4.11) was simplified to:

$$k = ln\frac{1}{(1-X_{DMF})} \times \frac{1}{\tau} \times \frac{1}{(O_2)^{0.38}} \qquad (4.13)$$

Table 13 shows the experimental conditions and calculated reaction rate constant values for different temperature effects where as expected the increase in reaction temperature resulted in higher rate constant.

Table 13: Rate constants for Arrhenius plot of temperature experiments.

Temperature (K)	Residence Time (s)	Oxygen Concentration (M)	Rate constant, *k* (s^{-1})
673.15	6	0.0875	0.861
698.15	6	0.0875	1.341
723.15	6	0.0875	1.414
748.15	6	0.0875	1.535
773.15	6	0.0875	1.520
798.15	6	0.0875	1.834

Then, to find the values of *Ea* and *A* for the new *k* values, Arrhenius plot for the natural logarithm of *k* versus 1/T was plotted as shown Figure 32. *Ea* was determined by multiplying the slop by the universal gas constant (8.314 J/mol.K) that gave 21998.8 J/mol and the value of pre-exponential factor (*A*) was calculated from ln *A*= intercept, and this gave $A= 2.4\times10^{5}\ M^{-0.38}\ s^{-1}$.

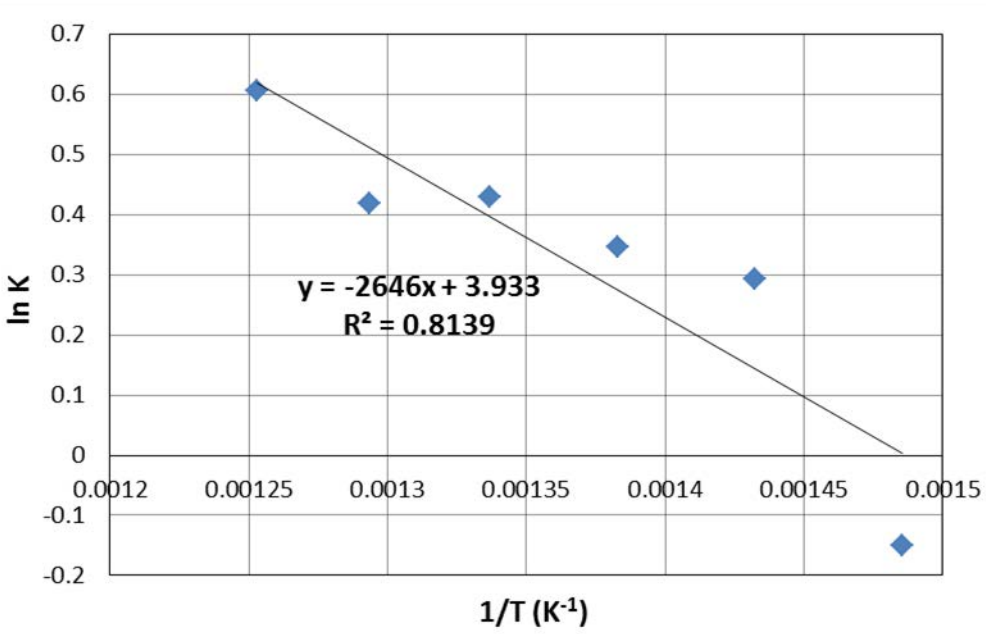


Figure 32: Arrhenius plot for DMF oxidation, P=250 bar.

Thus, the generated global rate expression for the destruction of DMF up to a temperature of 525°C is as follows:

$$rate = \frac{-d[TOC_{DMF}]}{dt} = 2.4 \times 10^5 \ (M^{-0.38}\ s^{-1})\ exp\left(-\frac{21998\frac{J}{mol}}{RT}\right)[TOC_{DMF}]\ [O_2]^{0.38} \qquad (4.14)$$

4.7 Summary

Kinetic analysis of SCWO of DMF showed the significant impact of IPA to reduce activation energy from 90.7 (in the absence of IPA) to 22 kJ/mol. This facilitates for faster reaction start up and better oxidation towards final products. Also, excess heat generated by adding IPA to reaction medium resulted in higher reaction rate constant and pre-exponential factor that also indicates faster oxidation rate. In this work, oxygen in the SCWO of DMF has an influence in which its order was 0.38, which is similar to other values as 0.36 and 0.4±0.1 that found in the literature (Kings, 2012, Al-Duri et al., 2008).

CHAPTER 5- SUPERCRITICAL WATER OXIDATION OF 1,8-DIAZABICYCLO[5.4.0]UNDEC-7-ENE (DBU)- PRELIMINARY STUDY

5.1 Introduction

This chapter illustrates the results and their discussion for the experiments that were carried out on the supercritical water oxidation of DBU as a preliminary study. The aim of this part was to study the oxidation of DBU in SCWO and the behaviour of ammonia as unwanted intermediate from DBU decomposition. This included investigating the effects of the typical operating conditions on the destruction of DBU such as temperature, initial DBU concentration, oxidant ratio and residence time. Furthermore, reaction kinetic study was also carried out and presented in this chapter. The main parameters used in this work to illustrate the performance of the process under studied conditions were total organic carbon removal (%TOC removal), total nitrogen removal (%TN removal) and yield of ammonia (%NH_4).

5.2 DBU Selection

1,8-Diazabicyclo[5.4.0]undec-7-ene, or DBU is a tertiary amine that belongs to the class of amidine compounds. It has a chemical formula of ($C_9H_{16}N_2$), which is complex due to its hetero-aromatic nature. It is mainly used as a catalyst in organic synthesis, such as a catalyst for polyurethane and for reactions of alicyclic and aliphatic isocyanates (NIST, 2016). In pharmaceuticals, it is employed for the synthesis of cephalosporin (anti-biotic) as a protecting agent. Also, it is used as a curing agent for epoxy and with Trimethylbenzene in fullerene purification in addition to its usage as a dehydrohalogenation agent.

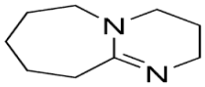
The physical properties of DBU (Sigma-Aldrich, UK, >99%) are given in table 14. It was slightly yellow liquid and showed complete miscibility in water during all runs. The stoichiometric equation for the complete oxidation of DBU in SCWO is shown below:

$$C_9H_{16}N_2 + 13\ O_2 \rightarrow 9\ CO_2 + 8\ H_2O + \ N_2 \quad (5.1)$$

Hydrogen peroxide thermal decomposition reaction is shown below:

$$H_2O_2 \ \rightarrow \frac{1}{2} O_2 + H_2O \quad (5.2)$$

Table 14: Physical properties of DBU (Chembook, 2015).

DBU , CAS number: 6674-22-2	
Structure	
Molecular formula	$C_9H_{16}N_2$
Appearance and solubility	Colourless liquid, miscible with water in all proportions and in the majority of organic liquids.
Molar mass	152.24 g/mole
Density	1.019 g/ml
Boiling point	115 ^oC
Melting point	-70 ^oC

The reasons of selecting DBU as a model pollutant compound in this study are listed below:

- DBU is a hazardous and a complex nitrogen-aromatic (hetero-cyclic) pollutant that is widely used in pharmaceutical and other wastewater sources, therefore the SCWO investigation of DBU is highly interesting. In addition, recently most of SCWO studies

have focused on the destruction of nitrogen-containing compounds due to their refractory nature (chemically stable; non-biodegradable in nature).

- Moreover, only a few studies on DBU treatability were conducted, consequently there is a need for more detailed studies to enrich the collective knowledge of DBU and to provide insight into the reactive behaviour of DBU and to obtain novel kinetic data.
- DBU represents a very important class of hetero-polycyclic pollutants that are more refractory and their presence even in low concentrations has become a great concern, in addition this study would enrich the field of the comparison with other simpler class of organics as nitro-aliphatic compounds as in case of DMF in Chapter 4.
- SCWO process is ideal to eliminate the hazard of this kind of aqueous wastes that is widely found in low concentrations in pharmaceutical effluents.

In summary, DBU as a chemically stable-nitrogenous compound was selected for the above mentioned reasons to conduct a preliminary study using SCWO as an alternative technology to treat such hazardous material. The results from this work are expected to give deep knowledge about SCWO applicability, DBU destruction behaviour and its reaction kinetics and would be the baseline for next step as in Chapter 6 where IPA was used to improve the process. In addition, the results are expected to allow for more understanding to the treatability of a more general class of complex nitrogen-containing pollutants and would help in the comparative study with simpler material as represented by DMF in Chapter 4.

5.3 Effect of System Operating Conditions

SCWO Process diagram, components and experimental procedures used in this chapter were previously described in Sections 3.1 and 3.2.

5.3.1 Experimental Work Plan

In this part, the SCWO of DBU in solutions with water was carried out at varying operating temperatures, DBU feed concentrations, oxidant stoichiometric ratios and residence times. During studying each variable individually, a temperature of 400^{o}C, 5 mM of DBU solution and delivering the stoichiometric amount of oxidant (1 SR) were used to avoid overlapping. The operating pressure during all runs was fixed at 250 bar as it has been widely reported that it has no effect on the process efficiency in supercritical region except to maintain the system in mono-phase system (Al-Duri et al., 2008). The ranges of the used operating conditions during this part were summarized in Table 15. Also, the justifications for selected ranges for every individual operating variable are explained in the subsequent sections.

Table 15: Summary of the operating conditions used in SCWO of DBU experiments.

Variable	Range	Fixed conditions
Temperature	400 - 525^{o}C	$[DBU]_o$ = 5 mM SR = 1SR
$[DBU]_o$	1-10 mM	Temp = 400 ^{o}C SR = 1SR
Oxygen Ratio	0.8 – 2 SR	Temp = 400 ^{o}C $[DBU]_o$ = 5mM
Residence time: 2-10 seconds for all experiments		

5.3.2 Effect of Residence Time

The investigated range of residence times was selected to be from 2 to 10 seconds in this part, where the maximum residence time of 10 seconds was to maintain the turbulent flow regime in the reactor and the minimum of 2 seconds was based on the ultimate flow rates the HPLC pumps can deliver. Also, this relies also on the used temperatures and generated total flow rates of oxidant and organic solution. During all runs, stabilisation time of 25-30 minutes was adequate to confirm obtaining accurate residence times as experiments were designed. In addition, steady state check before each chapter confirmed this. The results of the effect of residence time on the TOC removal of DBU oxidation are shown in Figure 33.

Generally, Figure 33 shows an increase in TOC removal of DBU with all residence times investigated. Expectedly, longer reaction time allows for more contact between organics and oxidant and thus for further oxidation. There was a remarkable TOC conversion during the early stages of oxidation, which indicates that most of the oxidation takes place at the reactor's front section. For example, the TOC removal was 82.2% at 400^{o}C and 2 seconds of residence time. This agrees with another study that showed most of TOC removal of organics occurred at a residence time less than 2 seconds (Cabeza et al., 2011). This rapid nature of SCWP process is due to the high solubility of reactants in SCW and high temperatures of this process. Then, the positive effect of residence time on TOC removal almost followed a consistent pattern with all temperatures investigated where a TOC removal of 88% and 99.2% was achieved at 400^{o}C and 500^{o}C, respectively and at 10 seconds of residence time. The graph shows a minor improvement in the TOC removal can be achieved beyond 10 seconds of residence time. However, obtaining low total flow rates or being out of turbulent regime restricts going higher than 10 seconds. Also, from an engineering point of view, using bigger system to improve the oxidation efficiency will

lead to more cost and control issues, where other conditions could be exploited at the same range of residence times.

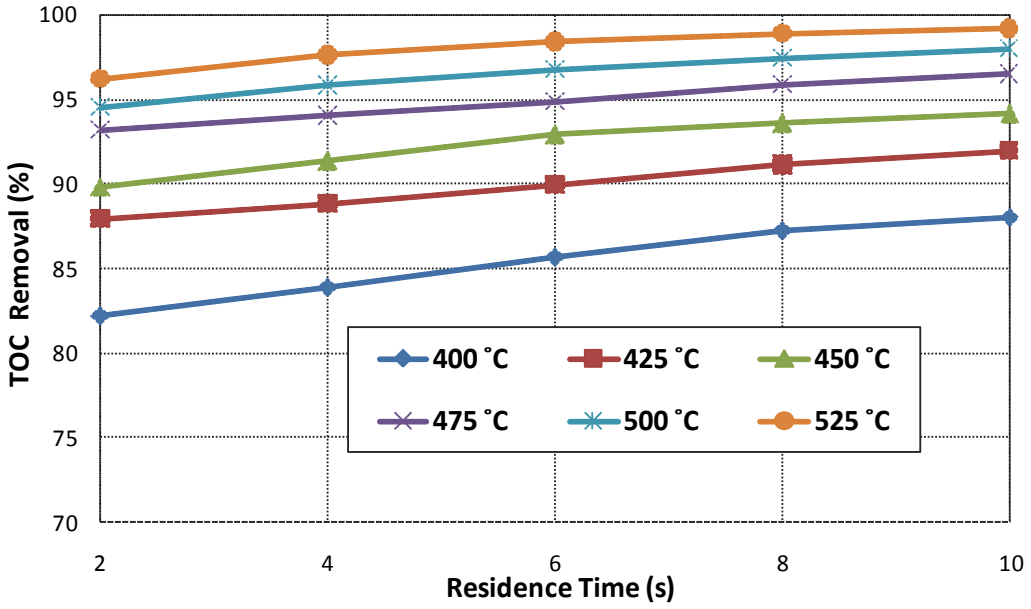


Figure 33: TOC removal against residence time at various temperatures. At 5 mM DBU, SR of 1 and 250 bar.

5.3.3 Effect of Operating Temperature

The effect of temperature on the SCWO of DBU was investigated in the range from 400^{o}C to 525^{o}C at initial DBU concentration of 5 mM, 1 SR, 250 bar and a residence time from 2 s to 10 s. This range of temperatures was selected based on the heating capacity of the used electric oven and since a temperature of 400^{o}C would guarantee that the reaction medium remains in mono-phase in all runs. Also, this range with 25^{o}C increment suits reaction kinetics as reaction rate is sensitive to temperatures.

Figure 34 shows the effect of temperature on TOC removal over the residence times investigated. There was a significant increase in TOC removal with temperature as the reaction

proceeded from 2-10 s during oxidation of DBU, which indicates the essential role of temperature to enhance organic material destruction. A similar role of temperature was observed with the oxidation of DMF in the previous chapter.

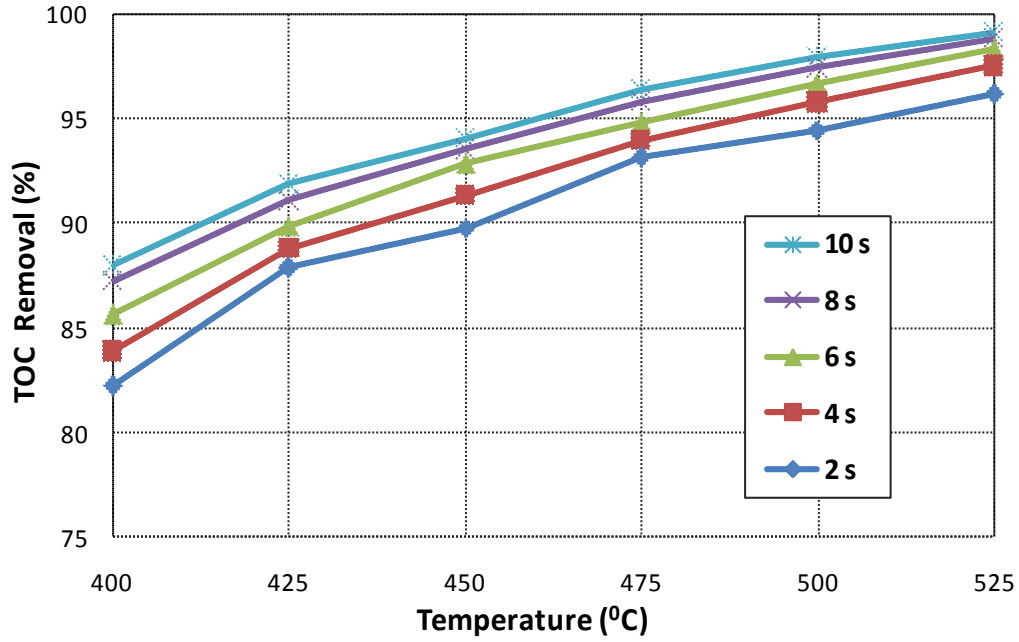


Figure 34: Effect of operating temperature on TOC removal at 5mM DBU, SR of 1, 250 bars and various residence times.

For example, TOC removal of DBU increased from 88 % at 400°C to 99.1% at 525°C that represents a 13% increase after 10 s residence time. Also, this maximum TOC removal of 99.1% shows that 525°C is high enough for complete DBU destruction even though it is a complex compound. The increase in temperature from 400°C to 525°C enhanced TOC removal by 17% at 2 s residence time, which is due to high reactant solubility in SCW, high temperature and fast radical generation. High TOC removal of 99.1% shows that temperature is the most influential variable on SCWO of DBU. These results agrees with another work that showed the TOC removal improved with the temperature, where a TOC conversion of >98% was achieved when DBU oxidised at 550°C, 2SR and at 7 seconds residence time (Al-Duri et al., 2008). Also, they

showed that DBU required higher temperature to be decomposed compared to DMF that 100% destroyed at 500^{o}C, which is due to its complex structure. Elevating one or a combination of other variables (e.g. reaction time, oxidant dosage and initial DBU concentration) could improve the destruction efficiency and minimise the needed operating temperatures, and thus improves the system economics.

Figure 35 shows the yield of nitrogenous species in the liquid phase as the temperature increases at 6 seconds of residence time. As with DMF oxidation, the figure shows that increasing the temperature from 400^{o}C to 525^{o}C increased the yield of ammonia. This trend of ammonia was observed with other works on DBU, who showed that higher temperatures are needed for the breakage of C-N bond during DBU oxidation (Al-Duri et al., 2008, Osibo, 2010). In this work, ammonia remained in the effluent with a yield of up to 65% at a temperature of 525^{o}C, where a similar value was obtained in Al-Duri et al's work. One study found that ammonia yield increased with temperature till 550^{o}C and then began to decrease during oxidising quinoline (Pinto et al., 2006a). Therefore, it's expected that ammonia would continue increasing until a sufficient high temperature is reached, and then would start decrease. Generally, temperatures in excess of 650^{o}C are needed to completely eliminate ammonia (Webley et al., 1991). However, the conditions used in this work seemed favoured for ammonia production if to be used for further applications such as in fertilizer industry. Nitrate (NO^{-3}) and nitrite (NO^{-2}) were at minimal levels as the temperature increased. Higher temperatures than those needed for ammonia are needed for their appearance and elimination afterwards.

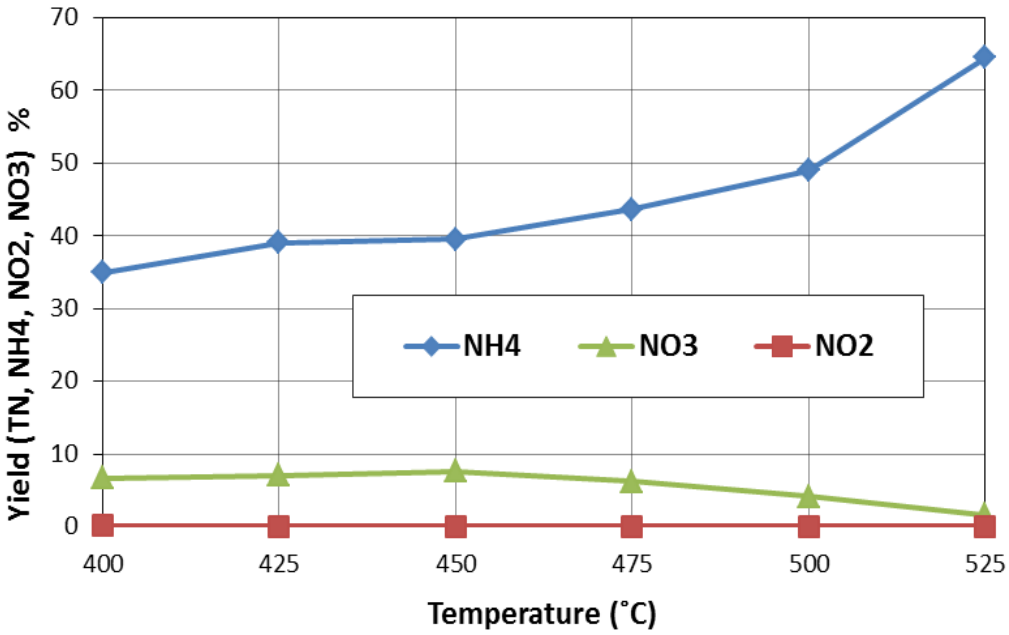


Figure 35: Nitrogen-Speciation yields as a function of temperature at 5mM DBU, SR of 1, 250 bar and 6 s.

Figure 36 shows a summary of all changes in the TOC and TN removals and in ammonia yield over investigated temperatures at 6 seconds of residence time. There was a steady improvement in TOC removal of around 3% with all temperatures as thoroughly illustrated in Figure 33. It shows also the similarity in the trend for both removals as carbon and nitrogen strongly bound to the organic material. However, the slight lower TN removal was due to the fact that nitrogen has more a complex chemistry especially in hetero-cyclic compound, which is the reason why more severe conditions are needed to eliminate unwanted nitrogenous by-products as in the case of ammonia. Moreover, it was obvious that treating DBU at relatively lower temperatures as from 400^{o}C to 525^{o}C allowed for ammonia generation, where these conditions can be utilized to produce ammonia for further applications. Therefore, more severe temperatures

as (>650^{o}C) are needed to completely eliminate ammonia, or using other approaches at milder temperature such as adding co-fuel or supplying more oxidant or using a longer residence time. Coupling high conversion of TN as 92.2% with ammonia yield indicated that a small amount of N remained in the liquid phase while most of initial organic N is converted to nitrogen gas. In general, the range of temperatures was influential for excellent TOC destruction while higher temperatures are needed to improve the elimination of ammonia.

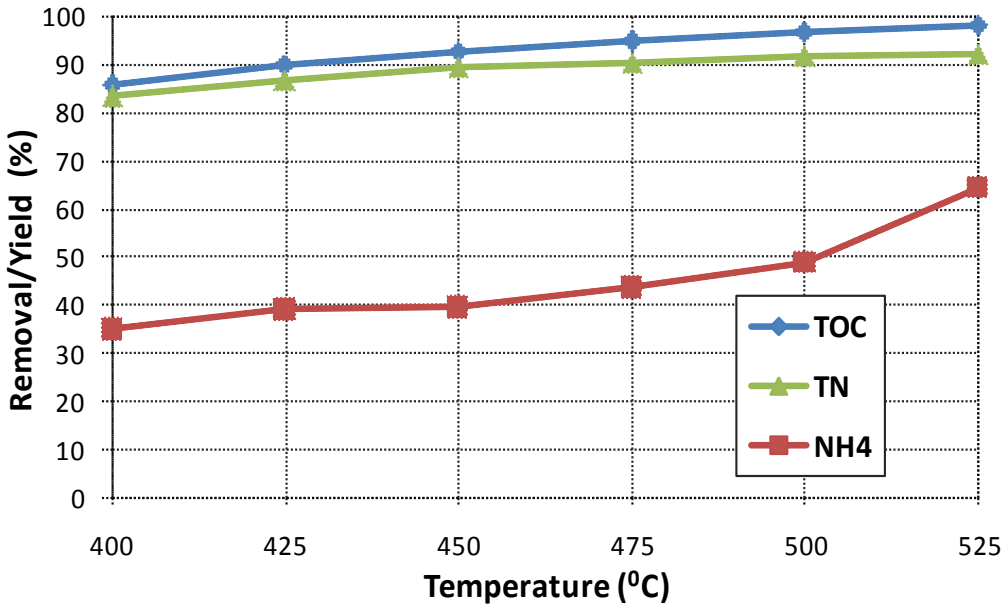


Figure 36: Effect of temperature on TOC, TN removals and NH4 yield at 5mM DBU, SR of 1, 250 bar and 6 s.

5.3.4 Effect of Initial DBU Concentration

It is essential to study the effect of organic concentration as reaction rate as a function of the content of reacting organic. Thus, the effect of DBU feed concentration on the oxidation of DBU was investigated at 400^{o}C, 1 SR, 250 bar and at a residence time from 2 s to 10 s. The

investigated initial DBU concentrations at reactor inlet were 1 mM, 2.5 mM, 5 mM, 7.5 mM and 10 mM. These concentrations at ambient conditions represent form 0.091 wt% to 0.91 wt% which mimic those that can be found in dilute industrial wastewaters. This range of DBU concentrations was selected to avoid any excess heat that may affect isothermal state of the used reactor and to avoid any precipitation. In addition, using this range would maintain the flow rates within the capacity of used HLPC pumps and guarantee obtaining turbulent flow regime in all runs based on the organic concentration selected, corresponding oxidant amount and temperature. Other conditions were kept at their minimal values during this section in order to avoid effects overlapping. The results of DBU concentration effect were presented in the form of TOC removal, TN removal and the yield of Nitrogen-speciation.

Figure 37 shows clearly the positive effect of DBU concentration on TOC removal at various residence times. As with DMF, increasing DBU concentration from 1 mM to 10 mM considerably and steadily enhanced the TOC removal. This general trend agrees also with other works that showed strong dependency between TOC destruction efficiency and TOC feed concentration (Qi et al., 2002, Al-Duri et al., 2008). The figure shows that the TOC removal improved from 53% at 1mM to 94.5% at 10 mM at 10 seconds of residence time, which represents 78.5% increase. Also, at 2 seconds the enhancement in the TOC removal was around 90% over the same range of DBU feed concentrations. Osibo found that the TOC removal increased with DBU feed concentration achieving a relatively similar TOC removal of 84% at similar conditions of 400, 7 mM, 1.25 SR, 250 bar and at 7 seconds of residence time (Osibo, 2010). This destruction enhancement was due to the fact that more organic content increases free radical generation in addition to the added enthalpy value to the feed. The figure also shows that there is still more capacity for SCWO by using organic above 10 mM, however, only up to this

concentration was used due to the low organic flow rates produced. Maximum TOC removal of 94.5% is a good achievement here due to using relatively low temperature of 400°C and 1SR of oxidant, thus with slightly higher conditions a better or even complete TOC removal could be achieved.

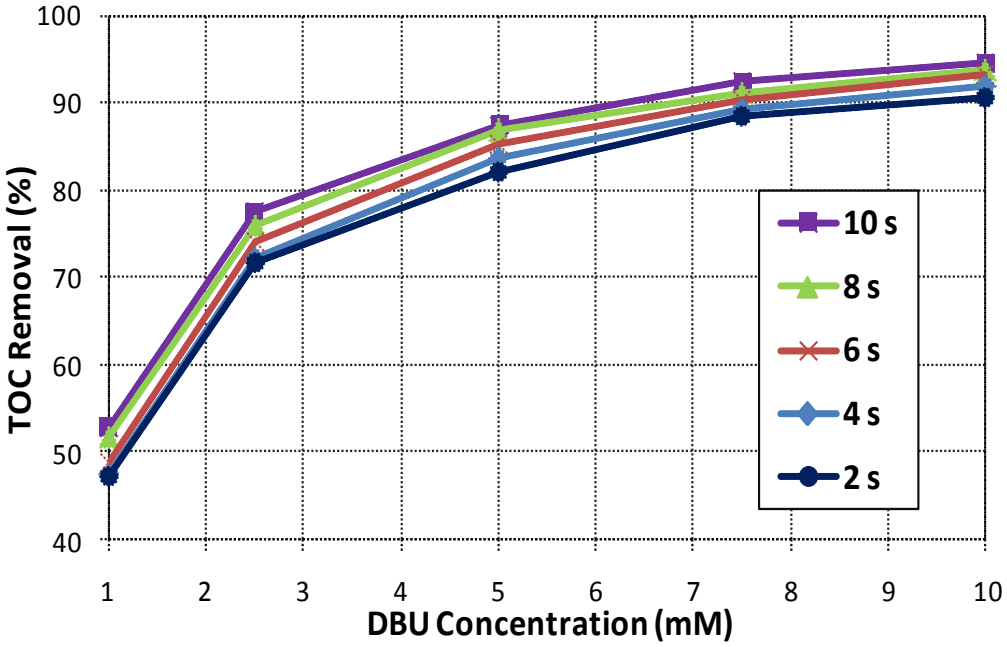


Figure 37: Effect of initial DBU concentration on TOC removal at 400°C, SR of 1, 250 bar and various residence times.

It was obvious that DBU concentration has an effect that is less than the influence of temperature on DBU oxidation, where the temperature is the most influential variable on SCWO process. Increasing residence time from 2 to 10 seconds in this set of experiments made an enhancement in the TOC removal by 12 % and 4% with DBU concentration of 1 mM and 10 mM, respectively.

Figure 38 illustrates the yield of nitrogenous species in the liquid phase as DBU feed concentration increased and at 6 seconds residence time. As with DMF, figure shows a gradual

increase in ammonia yield as initial DBU concentration increased from 1 to 10 mM. These results seem to be in contrast to those obtained in other work, where it was found that ammonia yield decreased with DBU feed concentration (Osibo, 2010). The author showed that the generated free radicals by increasing organic content enhances the TOC conversion and possibly inhibits ammonia formation as unwanted intermediate. Therefore, further investigation using a wider range of DBU concentrations is needed to make a definite conclusion on its effect on ammonia. In this work, ammonia was the main refractory nitrogen-intermediate from DBU decomposition and using 400^{o}C seemingly was not enough to show an obvious reduction. The levels of nitrite and nitrate were at their minimum values during investigated initial concentrations of DBU.

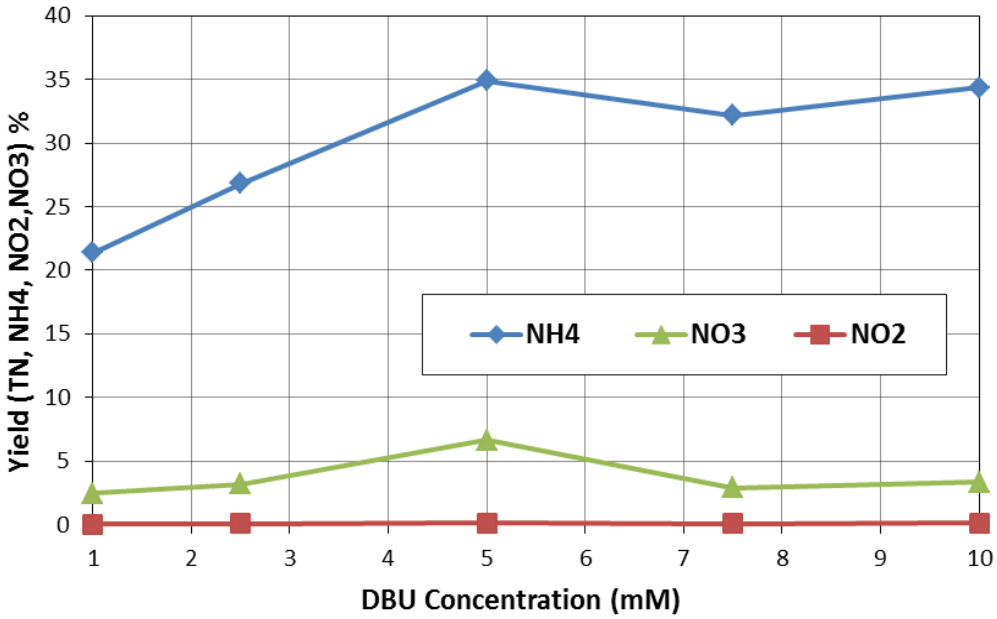


Figure 38: Nitrogen-Speciation yields as a function of DBU concentration at 400^{o}C, SR of 1, 250 bar and 6 s.

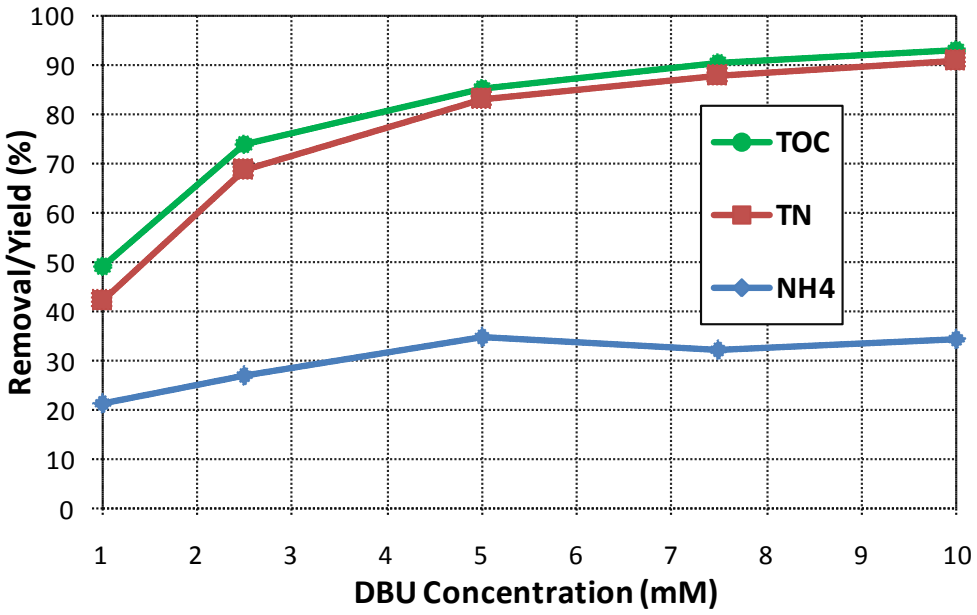


Figure 39: Effect of DBU concentration on TOC, TN removals and NH4 yield at 400°C, SR of 1, 250 bar and 6 s.

Figure 39 above shows a summary of all changes in the TOC and TN removals and in the yield of ammonia with investigated DBU concentrations at a residence time of 6 seconds. TOC and TN removals almost improved in the same manner as DBU content increased, and TN removal was slightly lower than that of TOC removal due to the complexity of nitrogen chemistry that indicates nitrogen always needs more severe conditions to eliminate its species as in case of ammonia. Although a high TN conversion of 91% was reached at 6 seconds of residence time, most of the remaining inorganic nitrogen in the liquid phase was in the form of ammonia, where more severe operating condition are needed for its elimination. Other approaches such adding co-fuel, more oxidant and/or longer residence time are other options to keep working under milder temperatures.

5.3.5 Effect of Oxidant Ratio

Supplying the needed amount of oxidant is essential during the treatment of organics in hydrothermal oxidation environment as in the case of DBU. Thus, the effect of oxidant ratio on DBU oxidation was investigated at various ratios from 0.8 SR to 2 SR, which represents 80% of needed oxidant to 100 % excess. This range of oxidant was selected to cover specific oxidant range, since more oxidant would not be favourable for large-scale application due the cost and control challenges. Moreover, the selected range of oxidant ratios was based on the controllable HPLC pump flow rates that were based on the corresponding DBU concentration selected and the temperature. Other conditions were kept at a temperature of 400^{o}C, initial DBU concentration of 5 mM, 250 bar and a residence times from 2-10 seconds. The results of oxidant stoichiometric ratio effect were presented in forms of TOC removal, TN removal and yields of Nitrogen-speciation.

Figure 40 shows the effect of different oxidant ratios on the TOC removal at various residence times. As with DMF oxidation, the figure shows an obvious increase in the TOC removal as oxidant ratio ranged from 0.8 to 2 SR over residence times investigated. For example, the TOC removal improved from a lower value of 85.6 % with 0.8 SR to 93.7 % with 2 SR after 10 seconds of residence time, which is around 10 % of increase. This observation is in agreement with another work that found increasing oxidant ratio enhanced TOC conversion into carbon dioxide during DBU oxidation at similar conditions (Al-Duri et al., 2008). Also, another work showed the positive dependence of TOC removal of quinoline (similar to DBU) on oxidant ratio at similar conditions, where almost 100% TOC conversion was obtained at an SR of 2.5, 550^{o}C and 8 seconds residence time using a similar system (Pinto et al., 2006a). They explained that this improvement is due to radical generation as oxidant supplied, and thus this enhances the

oxidation process. Moreover, the graph shows that unlike other works (Cocero et al., 2000a), oxidant ratio above 2 SR would continue to further enhance the removal. Achieving a maximum TOC removal of 93.7 % with 2SR is promising as it was obtained at relatively lower temperature of 400^{o}C and 5 mM DBU. This implies that better or even complete removal could be achieved by an optimum combination of temperature, oxidant ratio, organic concentration and residence time. This was proved in this work by an experiment that was carried out at 450^{o}C and using 1.25 SR, where the TOC removal improved to 96 % without the need for severe operating conditions. Also, extending the residence time to 12 seconds for the same experiment made a TOC removal of 96.3%.

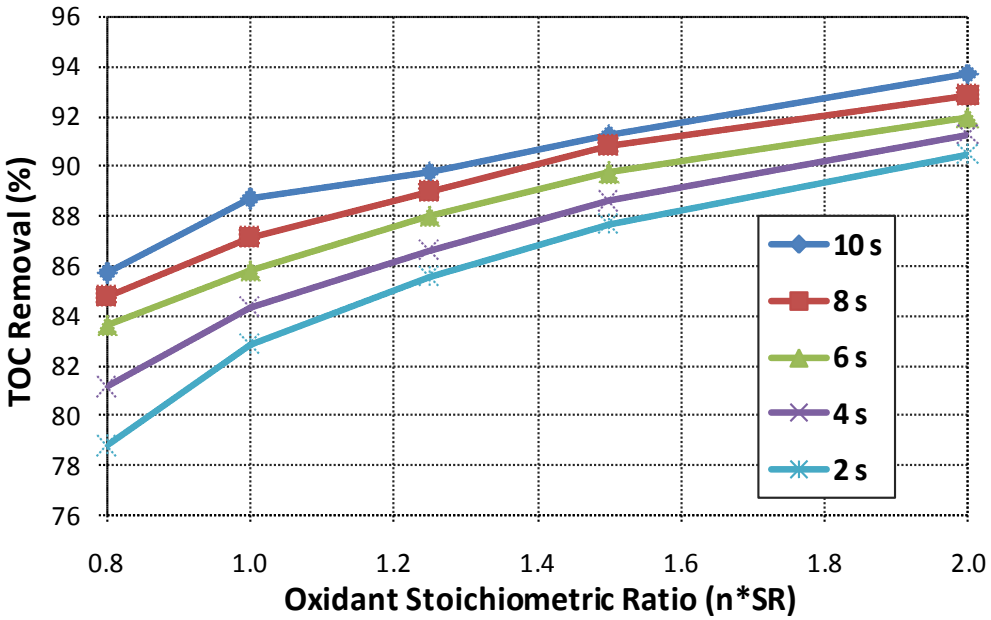


Figure 40: Effect of oxidant stoichiometric ratio on TOC removal at 400^{o}C, 5 mM DBU, 250 bar and various residence times.

Figure 41 displays the yield of nitrogen-speciation in the liquid phase with different oxidant ratios at 6 seconds residence time. It shows that increasing oxygen especially beyond an SR value of 1, considerably decreased the yield of ammonia. For example, as oxidant ratio increased from

1 SR to 2 SR, the yield of ammonia declined by 28%. Nitrite was at minimal levels, while nitrate decreased with oxidant where its yield was 3% with 2 SR. Ammonia trends in this work agrees with other works that found using excess oxygen is favoured for a better ammonia removal. Therefore, it has been suggested that using just a stoichiometric amount of oxygen is ideal in order to enhance ammonia removal and to obtain less nitrate and nitrite (Killilea et al., 1992, Cocero et al., 2000a, Oe et al., 2007). The observed reduction of ammonia, nitrite and nitrate with oxidant is a good sign that more nitrogen was converted towards gas phase in the form of N_2 even with milder temperatures used. However, using more oxidant with higher temperatures would enhance DBU and ammonia destruction further.

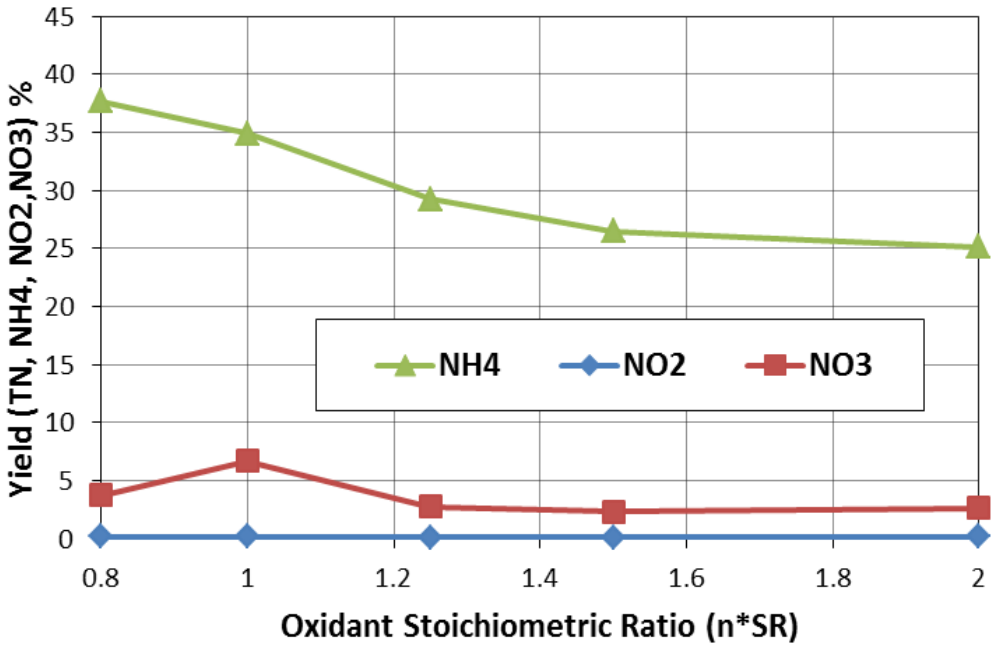


Figure 41: Nitrogen-Speciation yields as a function of oxidant stoichiometric ratio at 400°C, 5 mM DBU, 250 bar and 6 s.

A broader picture for TOC and TN removals in addition to the yield of ammonia is shown in figure 42. The figure shows the similarity in the destruction behaviour of TOC and TN and their trends indicate that oxygen attacks both in the same manner. TN removal was slightly less than

that of TOC due to the complex chemistry of nitrogen compared to the carbon. Increasing oxygen dosage obviously reduced ammonia yield, where combining the TN removal of 91% with ammonia yield, indicates the positive role of oxidant to shift the reaction forward into gaseous species despite relatively low temperature used in this section.

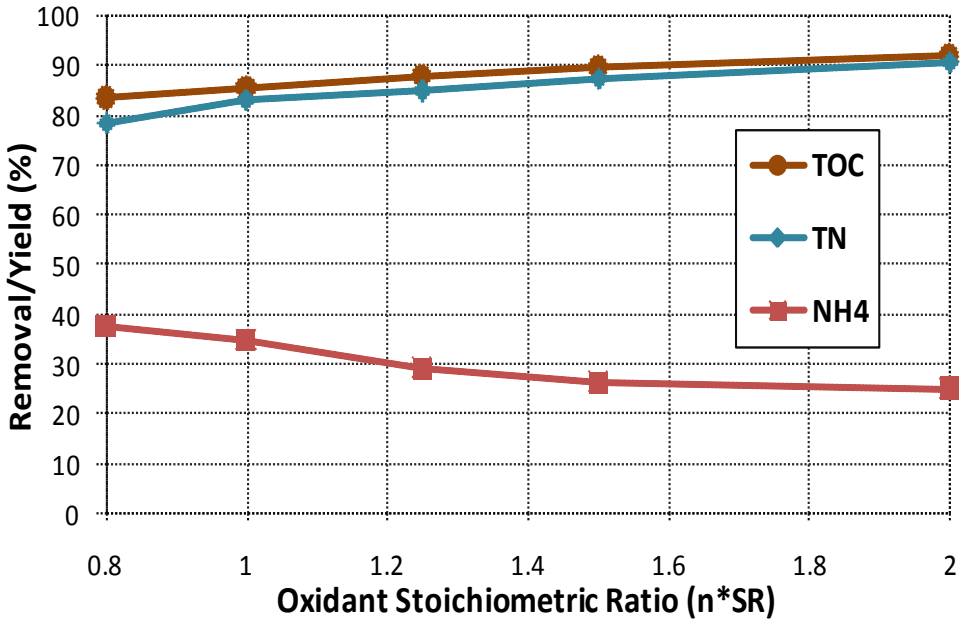


Figure 42: Effect of oxidant stoichiometric ratio on TOC, TN removals and NH4 yield at 400°C, 5 mM DBU, 250 bar and 6 s.

5.4 Summary

Although DBU is a complex organic compound, temperature was a very influential variable to destroy DBU, where maximum TOC removal of 99.1% was achieved at 525^{o}C. Investigating temperatures up to 525^{o}C did not decrease the produced intermediate ammonia where higher range of temperatures is needed. Also, results showed that the temperature effectively destroys the carbon pathway, while nitrogen needs more severe conditions. Temperature was followed by the effect of organic initial concentration that positively improved the TOC removal with a maximum TOC removal of 94.5%, while ammonia remained stable. Finally, oxidant ratio effectively enhanced the TOC with a maximum TOC removal of 93.7% and decreased the yield of ammonia even though low temperature of 400^{o}C was used. The considerable destruction at early stages of hydrothermal process is due to the rapid nature of oxidation reactions, which is due to high solubility in SCW and high reaction temperatures of SCWO. Elevating and optimizing the operating conditions could achieve a better organic removal and lower ammonia yield at milder conditions. Also, using a novel approach such as adding co-fuel may help to minimize conditions needed to achieve destruction.

5.5 Global Kinetics of DBU Oxidation

In the absence of detailed reaction mechanisms, quantifying the global reaction rate by identifying the main SCWO pathways is sufficient for engineering design purposes. The type and amount of formed intermediates during oxidation reaction also influence the reaction rate in addition to the role of starting organic material. Moreover, the oxidant ratio also influences the reaction rate and mechanism. The qualitative investigation of the effects of different process

variables as temperature, organic concentration, oxidant ratio and residence time on DBU decomposition kinetics was performed as previously illustrated in Section 5.3.

To study quantitatively the effects of these parameters, kinetic analysis was conducted to find the reaction rate parameters, namely the reaction rate constant (k), the Arrhenius parameters, namely the pre-exponential factor (A), activation energy (Ea) and the orders of reaction with respect to DBU (a), oxidant (b) and water (c) using global power-rate law expression. Several SCWO kinetic studies have been carried out (as explained in literature survey) either on waste mixtures or on single compounds under different conditions of temperatures, residence times, organic concentrations and with using different reactor designs. The studies then presented kinetic parameters and the global rate-law expressions. Most of SCWO kinetic models have been developed from the global rate law expression as in equation (5.4) below:

$$\frac{-d[Organic]}{dt} = K[organic]^a[oxidant]^b[H_2O]^c = A\exp^{\left(-\frac{Ea}{RT}\right)}\ [organic]^a[oxidant]^b[H_2O]^c \quad (5.4)$$

Where

k= Reaction rate constant in $M^{1-a-b-c}\ s^{-1}$

[organic] = organic compound initial concentration (mol/L) at reactor entry

[oxidant]= oxidant initial concentration (mol/L) at reactor entry

A = Pre-exponential factor in $M^{1-a-b-c}\ s^{-1}$

E_a = activation energy in J/mol

R = Universal gas constant (8.314 J/mol.K)

T = Reaction temperature (K)

a = Reaction order with respect to the reactant organic compound

b= Reaction order with respect to the oxidant

c= Reaction order with respect to the water

In this study, the kinetic analysis was performed by fitting the obtained experimental data to the global power law by two steps:

- Pseudo –first-order approximation

- Integral method approximation

Water as a reaction medium for the SCWO of DBU was always represents more than 99% of medium (in excess), therefore the concentration of water was considered constant that has no effect on the DBU oxidation rate. Thus, reaction order with respect to water is zero.

5.5.1 Pseudo-First-Order Approximation

The global kinetics for SCWO of organic wastewaters have been described by several researchers by pseudo-first-order expression, that expresses a reaction of order of one with respect to the organic and zero with respect to oxygen (Helling and Tester, 1988, Pinto et al., 2006b, Abelleira et al., 2013). This is a good initial simplification as the oxygen used in all runs was always in excess to ensure completely oxidising DBU. This makes the global power-rate law expression as follows:

$$rate = \frac{-d[DBU]}{dt} = k[DBU] \qquad (5.5)$$

And since TOC values are the main experimental conversion data, the equation was modified to be:

$$rate = \frac{-d[TOC_{DBU}]}{dt} = K[\mathrm{TOC}_{DBU}] \qquad (5.6)$$

By integrating equation 5.6 gives equation (5.7) at any given temperature;

$$\ln\left(\frac{[\mathrm{TOC}]}{[\mathrm{TOCo}]}\right) = -Kt \qquad (5.7)$$

Ln ([TOC]/[TOC_o]) can then be plotted against time (t) for each temperature to obtain k from the slope. Figure 43 illustrates this.

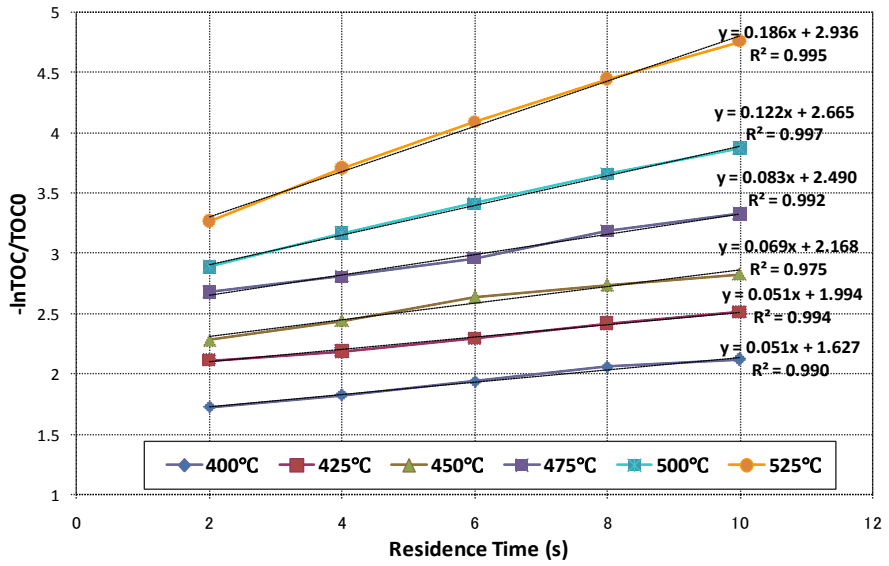


Figure 43: Natural logarithm of (TOC/TOC_o) versus residence time for DBU experiments at studied temperatures and a pressure of 250 bar.

In order to determine Arrhenius parameters as activation energy (*Ea*) and pre-exponential factor (*A*), the natural logarithm of obtained rate constant (*k*) for each temperature was plotted versus temperature inverse (1/T) as shown in Figure 44.

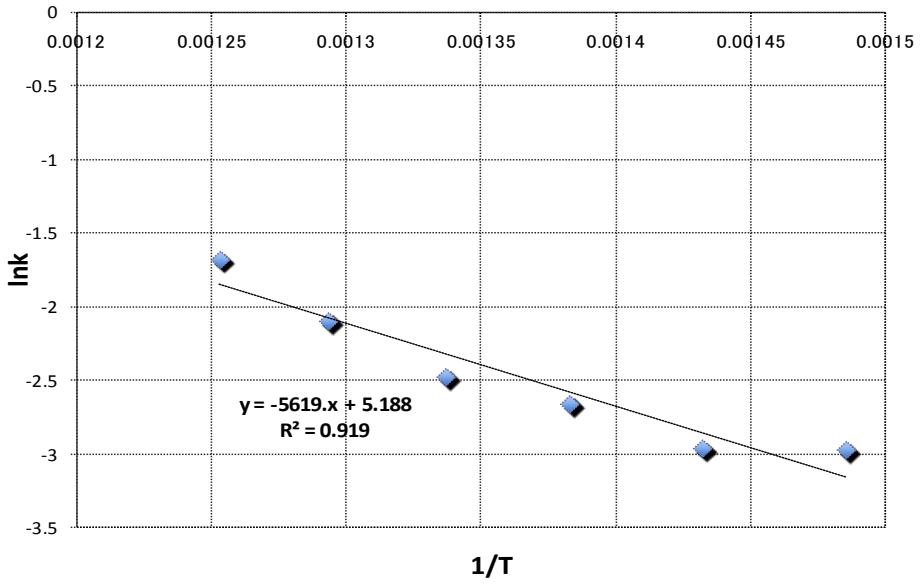


Figure 44: Arrhenius plot for the oxidation of DBU.

Therefore, the value of activation energy was determined by multiplying the slope (5619) by the universal gas constant (8.314 J/mol.K), which gave *Ea*=46722.2 J/mol and the value of pre-exponential factor was calculated from ln *A*= intercept, and this gave *A*=179.2 s^{-1}. Therefore, the emerged Pseudo-first-order rate expression for the oxidation of DBU at the temperatures investigated is given by:

$$rate = \frac{-d[TOC_{DBU}]}{dt} = 179.2\ (s^{-1}) \exp\left(-\frac{46722.2\ J/mol}{RT}\right)[TOC_{DBU}] \qquad (5.8)$$

5.5.2 Integral method approximation

To understand more of the development of the global rate expression for DBU oxidation, integral method approximation was used to mathematically express the kinetic data. To determine the global kinetic parameters for DBU oxidation equation (5.4) was used by considering that the order of DBU equal to one. These parameters were regressed from the complete set of data to predict the reaction rate of DBU oxidation over the conditions investigated and by assuming that the destruction of DBU is only a function of temperature, DBU and oxygen concentrations as

water was always in excess amount (>99% water). Although some works of oxidation kinetics in SCWO suggested that the oxygen has a minor effect or an order of zero (as previously discussed), it is worth discovering any influence of oxygen concentration on the DBU destruction. Therefore, oxidant effect experiments were carried out at 400°C, 5 mM DBU concentration, 250 bar and with five oxidant ratios (from 0.8 SR to 2 SR) that represent from 52 mM to 130 mM oxidant concentration at reactor inlet. The TOC removal for these experiments was shown in figure 40 in Section 5.3.5. It showed obviously an increase in the TOC removal as oxygen concentration increased. Thus, the order of reaction with respect to oxygen should be higher than zero and then the previous assumption (Pseudo-first order approximation) for DBU destruction needs to be improved. Therefore, the PFR design equation was used to determine the order of oxygen using integral method approximation with a=1 and b > zero where equation 5.4 can be rearranged as below:

$$(-rA) = \frac{-d[DBU]}{dt} = k[DBU][O_2]^b = A\,exp^{\left(-\frac{Ea}{RT}\right)}\,[DBU][O_2]^b \qquad (5.9)$$

The concentration of oxidant can be assumed constant ($[O_2]=[O_2]_o$). The performance equation for steady-state plug flow reactor was applied (Levenspiel, 1999) as follows:

$$\frac{\tau}{[DBU]_O} = \int_0^X \frac{dX_{DBU}}{(-rA)} \qquad (5.10)$$

Where $\boldsymbol{\tau}$ is the residence time, [DBU]o is the DBU initial concentration, X_A is the conversion of DBU and $(-r_A)$ is the reaction rate for the SCWO of DBU. Substituting equation 5.9 into equation 5.10 yielded the following equation:

$$\ln\left(\frac{1}{(1-X_{DBU})}\right) = k.t[O_2]_o^b \qquad (5.11)$$

Thus, to determine the numerical estimate of b, ln[1/(1-X)] versus $\boldsymbol{\tau}$ was plotted for oxidant experiments. Then, the slopes produced $k[O_2]_o^b$ as shown in Figure 45.

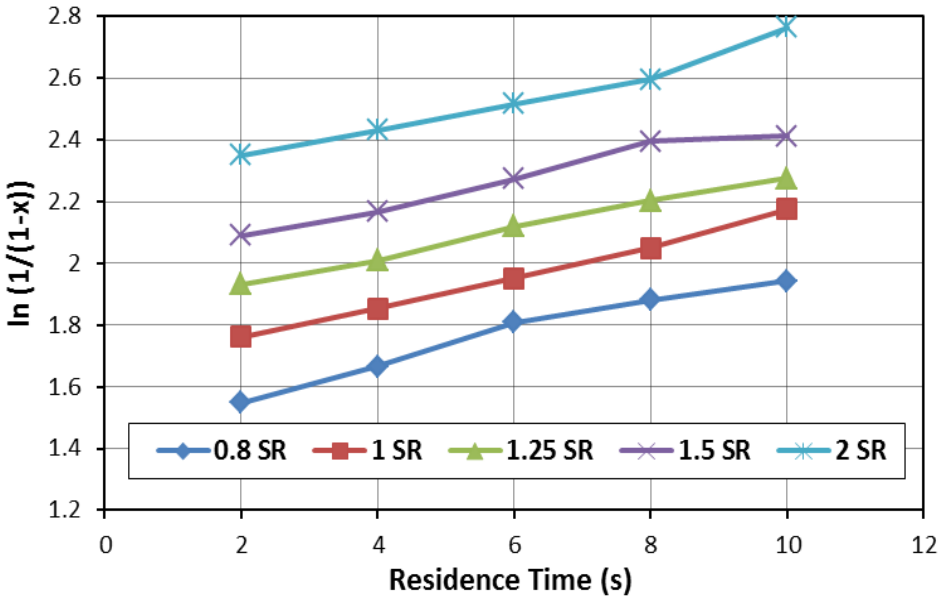


Figure 45: Natural logarithm of (1/(1-X)) versus residence time for DBU experiments with varying oxidant concentrations.

By taking the natural logarithm of $k[O_2]_o^b$, this term can be written as:

$$ln(k[O_2]_o^b) = ln\,(k) + b\,ln\,([O_2]_o) \qquad (5.12)$$

Therefore, plotting these slopes ($k[O_2]_o^b$) from Figure 45 as a function of the oxygen concentration on a logarithmic scale will produce a straight line with a gradient of *b* as shown in Figure 46.

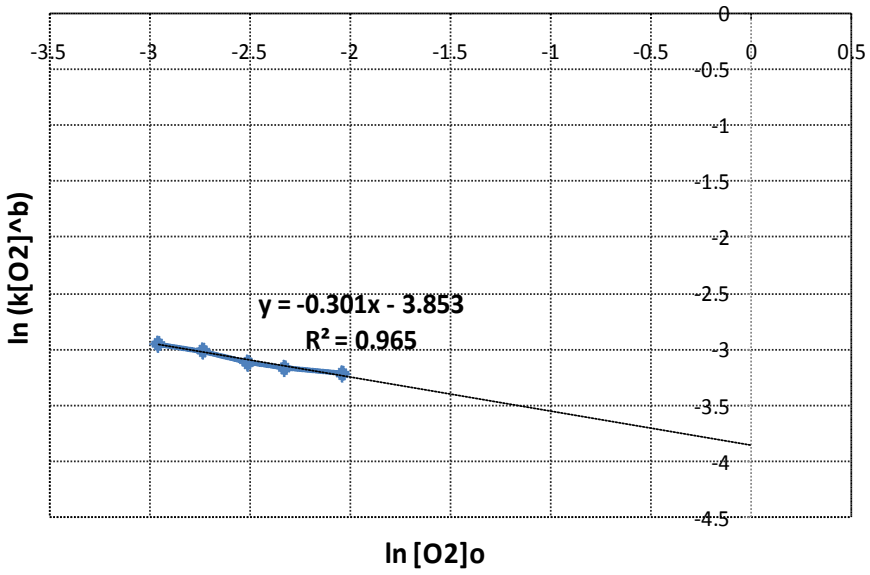


Figure 46: Determination of oxygen reaction order.

The slope of the straight line was 0.30 which is the order of reaction with respect to oxygen. By determination of the reaction orders for the global rate law for DBU and oxygen as (a=1 and b=0.3), to determine the values of k previous equation (5.11) was simplified to:

$$k = ln\frac{1}{(1-X_{BDU})} \times \frac{1}{\tau} \times \frac{1}{[O2]^{0.3}} \qquad (5.13)$$

Then, the values of reaction rate constants were calculated using conversion data for different temperature effects where as expected the increase in reaction temperature resulted in higher rate constant. Then, to find the values of *Ea* and *A* for the new *ki* values, Arrhenius plot for the natural logarithm of k versus 1/T was plotted as shown Figure 47. *Ea* and *A* were determined to be 25706.9 J/mol and 71.95 $M^{-0.3}$ s^{-1} respectively.

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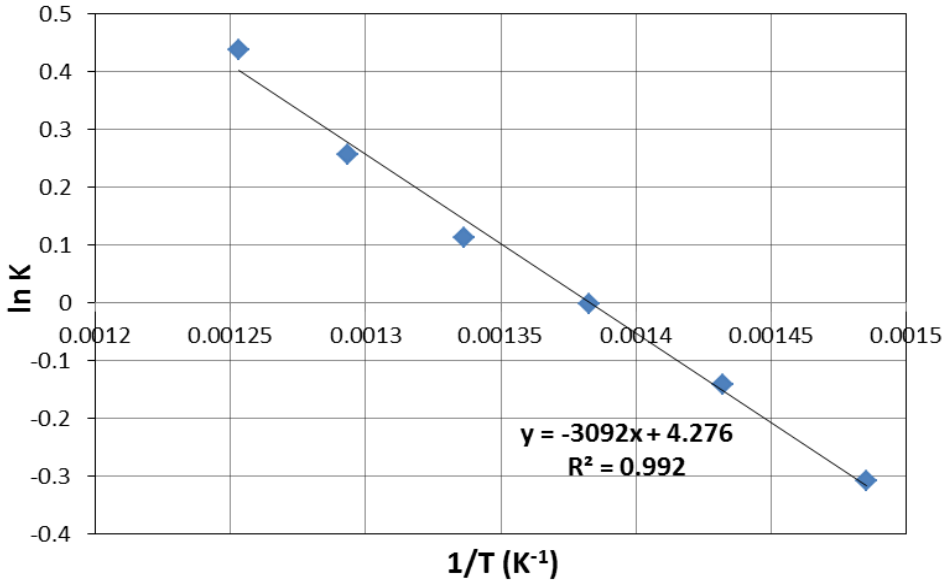


Figure 47: Arrhenius plot for DBU oxidation, P=250 bar.

Thus, the generated global rate expression for the destruction of DBU up to a temperature of 525°C is as follows:

$$rate = \frac{-d[TOC_{DBU}]}{dt} = 71.95\ (M^{-0.3}\ s^{-1})\ exp\left(-\frac{25706.9\ \frac{J}{mol}}{RT}\right)[TOC_{DBU}]\,[O2]^{0.3} \qquad (5.14)$$

5.6 Summary

Kinetic analysis of DBU oxidation in SCW showed activation energy of 25.7 kJ/mol. Using integral method approximation was more suitable to describe the kinetics of DBU, where the oxidant was found to have an influence on DBU destruction with an order of 0.3. This order agrees with another range of 0.4±0.1 that was found in the literature (Al-Duri et al., 2008).

CHAPTER 6- SUPERCRITICAL WATER OXIDATION OF 1,8-DIAZABICYCLO[5.4.0]UNDEC-7-ENE (DBU) IN PRESENCE OF ISOPROPYL ALCOHOL (IPA)

6.1 Introduction

This chapter illustrates the results and their discussion for the experiments that were performed to study the Supercritical Water Oxidation of DBU in the presence of Isopropyl alcohol (IPA). The aim of this work was to study the potential improvement in SCWO of DBU by adding IPA compared to IPA free system and in terms of DBU destruction and reaction kinetic parameters. This includes investigating the effects of the typical operating conditions on the system such as temperature, initial DBU concentration, oxidant ratio, residence time (all in presence of IPA) in addition to IPA feed concentration. Furthermore, the effect of co-fuel on ammonia yield as undesired intermediate and its ability to minimise the system operating temperatures was evaluated. The main parameters that were used in this work to show the performance of the process under studied conditions were total organic carbon removal (%TOC removal), total nitrogen removal (%TN removal) and yield of ammonia (%NH_4).

6.2 DBU Selection

The reasons for selecting DBU as a model pollutant compound in this study in addition to its uses and physical properties are shown in Chapter 5, Section 5.2.

The stoichiometric equations for the complete oxidation of DBU in SCWO in the presence of IPA in addition to hydrogen peroxide decomposition reaction are shown below:

$$C_9H_{16}N_2 + C_3H_8O + 17.5\ O_2 \rightarrow 12\ CO_2 + 12\ H_2O + N_2 \quad (6.1)$$

$$H_2O_2 \rightarrow \frac{1}{2} O_2 + H_2O \quad (6.2)$$

6.3 IPA Selection

Details about the reasons of selecting Isopropyl alcohol (IPA) as a co-fuel in this work in addition to its physical properties are explained in Chapter 4, Section 4.3.

The results of this work are expected to give a better knowledge about SCWO technology applicability, DBU destruction behaviour and its reaction kinetics in the presence of IPA as a novel approach to enhance the process. Furthermore, the obtained results would assess the effect of adding IPA as a co-fuel on ammonia reduction as unwanted intermediate and on minimising the severe conditions needed especially when a complex pollutant is under treatment. In addition, these results are expected to give a comparative study between the treatability of complex nitrogen-containing pollutants with simpler material as represented by DMF in Chapter 4.

6.4 Effect of System Operating Conditions

SCWO Process diagram, components and experimental procedures used in this chapter were previously described in Sections 3.1 and 3.2.

6.4.1 Experimental Work Plan

In this part, the SCWO of DBU solutions in the presence of IPA was carried out at the same operating conditions used in Chapter 5. During investigating IPA effect, initial IPA concentrations of 0.5 mM to 20 mM for IPA in the solutions were used to make a wide range of

IPA/DBU ratios such as from 0.1 to 4. The maximum concentration of DBU and IPA solutions in all experiments was 1.27 wt% which is suitable to avoid any excess heat and to maintain flow rates within the used HLPC pump capacities. The ranges of all used operating conditions during this part are summarised in Table 16.

Table 16: Summary of the operating conditions used in SCWO of DBU experiments in presence of IPA.

Variable	Range	Fixed conditions
Temperature	400 - 525 ^{o}C	$[DBU]_o$ = 5 mM $[IPA]_o$ = 5 mM SR = 1SR
$[DBU]_o$	1-10 mM	Temperature = 400 ^{o}C $[IPA]_o$ = 1-10mM, IPA/DBU ratio=1 SR = 1SR
$[IPA]_o$	1-20 mM	Temperature = 400 ^{o}C $[DBU]_o$ = 5 mM SR = 1SR
Oxygen ratio	0.8 – 2 SR	Temperature = 400 ^{o}C $[DBU]_o$ = 5mM $[IPA]_o$ = 5 mM
Residence time: 2-10 seconds for all experiments		

6.4.2 Effect of Residence Time

The effect of residence time on DBU oxidation was studied and shown as in Figure 48 in the form of TOC removal. Besides, the positive effect of residence time on the TOC removal that

previously explained in Section (5.3.2), the graph also shows the effect of residence time with and without IPA (round dotted lines) at investigated temperatures. For example, as the residence time increased from 2 to 10 seconds the TOC removal improved by 7%, 4% and 3% at 400°C, 450°C and 525°C, respectively. Using longer residence times higher than 10 seconds also could make further improvement, however, obtaining uncontrollable low flow rates and non-turbulent flow prohibited going higher than 10 seconds in this work. Achieving a TOC removal of 82.2 % at 2 s of reaction with 400°C shows the rapid nature of SCWO reaction.

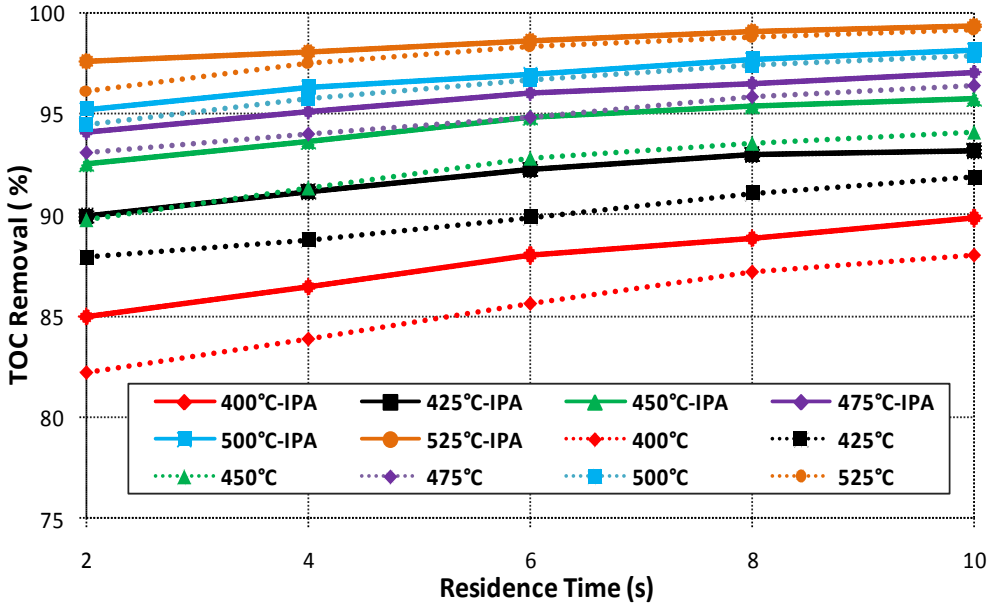


Figure 48: TOC removal against residence time at various temperatures, with and w/o IPA at 5 mM DBU, SR of 1, 250 bar.

6.4.3 Effect of Operating Temperature

Figure 49 shows clearly how adding IPA improved the TOC removal over all temperatures investigated. In other words, the presence of IPA aided the role of oxidation by generating extra heat from within the system. The improvement was significant mainly at lower temperatures as from 400 to 475°C and was acceptable at higher temperatures from 500°C and beyond. For

example, at 400°C the TOC removal improved by around 3% up to 89.8% when IPA added. At 525°C the presence of IPA improved the TOC removal to reach 99.4% as maximum destruction value although DBU is a complex compound. It is noteworthy that only 5 mM of IPA was used in this part of this work (IPA/DBU ratio of 1). Therefore, using higher ratios of IPA would achieve a better or even complete destruction for the organic material at equal or lower temperature as the extra heat generated from IPA oxidation reduces the required temperature for oxidation reaction. In general, adding IPA is a good option for SCWO system due to its rapid oxidation and generating free radicals that enhance the destruction further in addition to providing system with excess heat when it is used in higher concentrations.

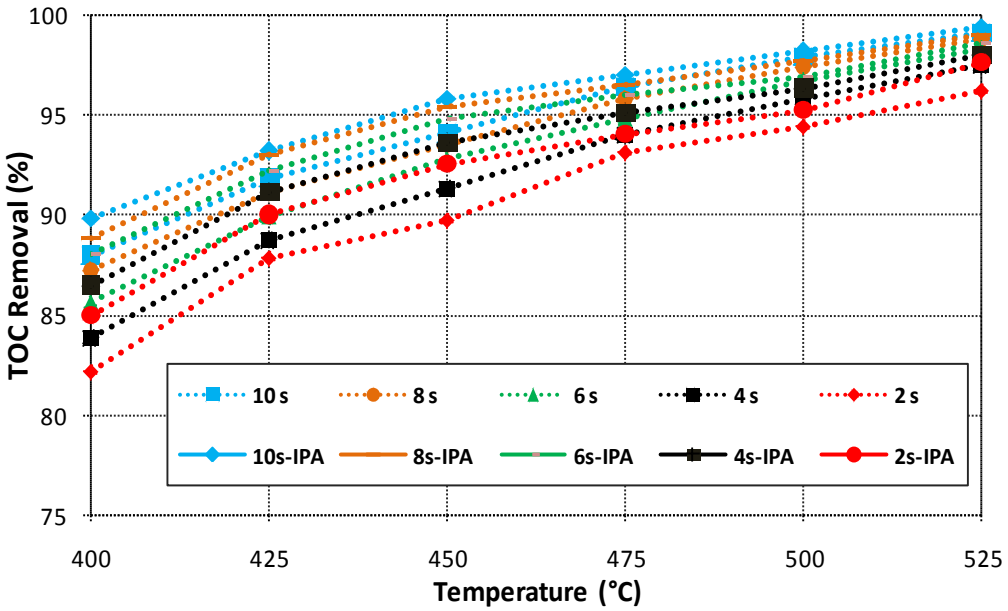


Figure 49: Effect of operating temperature on TOC removal at 5 mM DBU, with and w/o IPA, SR of 1, 250 bar and various residence times.

The effect of varying temperatures on the yield of nitrogen-speciation with and without IPA is shown in Figure 50. In general, it shows at all temperatures investigated that the presence of IPA clearly decreased the yield of ammonia and nitrate. Nitrite was always at its minimum values in both cases. Solid lines represent the effect of IPA when added compared to non-IPA runs

(round dot lines). For example, at 6 seconds of residence time adding IPA decreased the yield of ammonia by 25% at 400°C and by around 10% at 525°C in the presence of IPA. This obviously proves the positive influence of IPA to minimise nitrogen-product yields especially ammonia, which is the most refractory and unwanted intermediate. Thus, using higher ratios of IPA with similar or maybe slightly higher temperatures would help to decompose ammonia and at temperatures lower than actually needed.

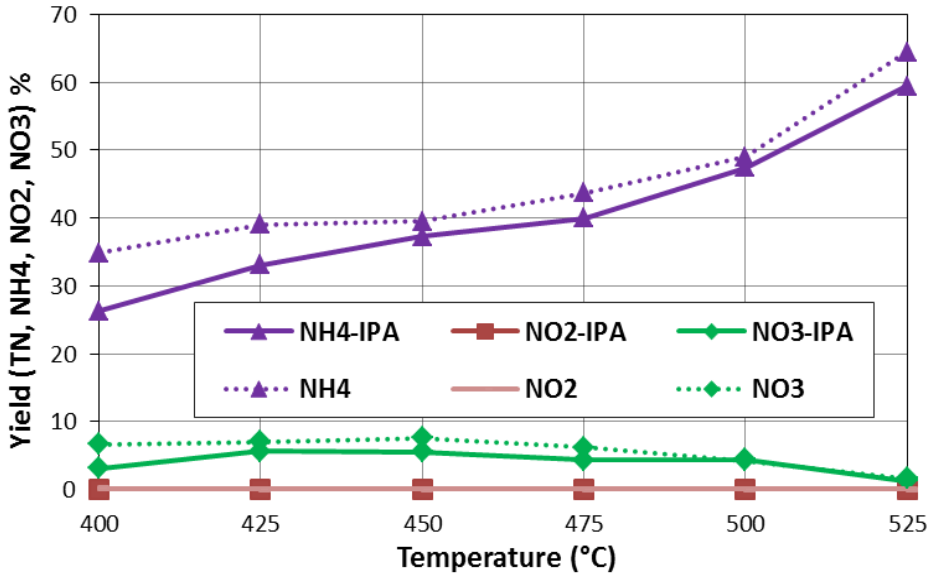


Figure 50: Nitrogen-Speciation yields as a function of temperature at 5 mM DBU, with and w/o IPA, SR of 1, 250 bar and 6 s.

Finally, Figure 51 illustrates a summary of the temperature effect on the removals and yield of ammonia at 6 seconds of reaction in the presence and absence of IPA. Besides, the positive effect of IPA on TOC removal as discussed in Figure 49, the presence of IPA also improved TN removal in a similar manner. For example, at 6 seconds of residence time the TN removal enhanced by around 4% at 400°C when IPA was added. The figure shows that treating DBU at temperatures below 525°C still did not decompose ammonia effectively, while this range of temperatures allowed for ammonia generation. However, the presence of IPA minimised the

yield of ammonia with all temperatures studied as shown in Figure 50. Therefore, using higher ratios of IPA would make further reduction in ammonia yield and thus significant ammonia destruction could be obtained at lower temperatures than 650°C. Also, supplying more oxidant is another option. This is supported by that presence of IPA improved the conversion of TN from 92.23% to 94.6% at 525°C and at 6 seconds of residence time that indicates that a small amount of initial TN remained unconverted in the liquid phase while most of initial TN converted to N_2. This range of temperature was enough for excellent DBU destruction especially through carbon component, however, higher temperatures or more co-fuel are still needed for a better removal for nitrogen pathway.

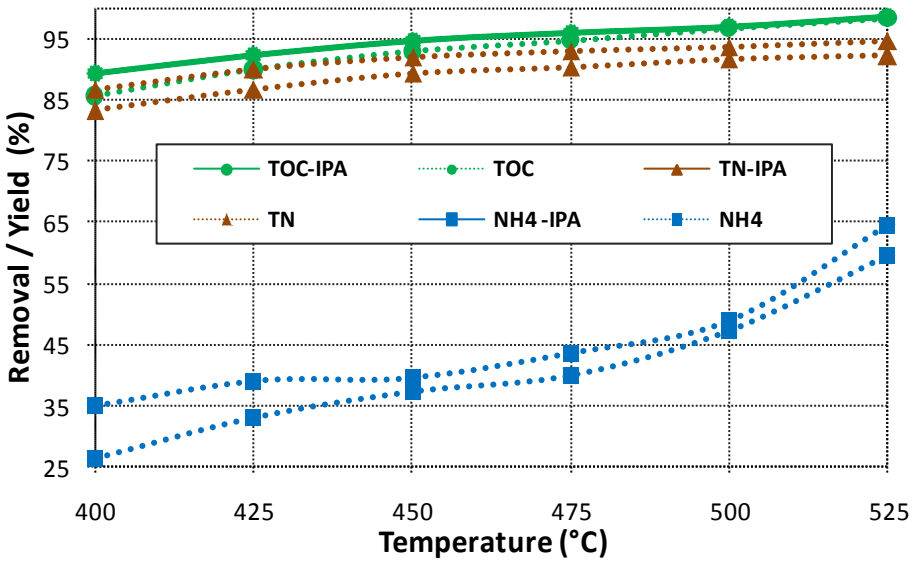


Figure 51: Effect of temperature on TOC, TN removals and NH_4 yield with and without IPA at 5mM DBU, SR of 1, 250 bar and 6 s.

6.4.4 Effect of DBU Concentration

Figure 52 shows the effect of initial DBU concentration with and without IPA at three selected residence times. The ratio of IPA/DBU was kept at 1 with all DBU concentrations studied. Besides, the positive effect of increasing DBU feed concentration on TOC removal as discussed in Section (5.3.4), the figure shows that the presence of IPA significantly enhanced the TOC conversion with all DBU concentrations investigated. For example, with adding the stoichiometric amount of IPA (i.e 1mM IPA) to 1mM of DBU an enhancement of 18% in the TOC removal was obtained over all residence times studied. Also, the enhancement was around 8% with 2.5 mM of DBU in the presence of stoichiometric IPA. The maximum TOC removal obtained in the presence of IPA was 95.3% with 10 mM of DBU and at 10 seconds of residence time. It is noteworthy that all this improvement obtained with a lower temperature of 400°C and using only a ratio of 1 for IPA/DBU, thus more IPA would enhance the destruction further.

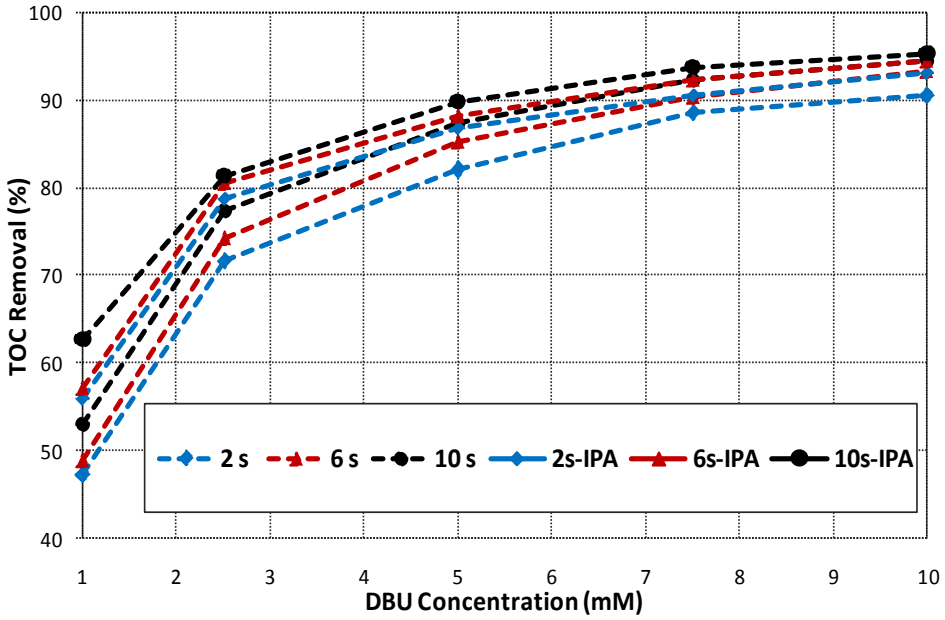


Figure 52: Effect of initial DBU concentration on TOC removal at 400°C, SR of 1, with and w/o IPA, 250 bar and various residence times.

Figure 53 shows the effect of different initial DBU concentrations on the yield of nitrogen-speciation in the presence of IPA compared to non-IPA system that previously discussed in Section (5.3.4). The figure shows clearly how the presence of IPA decreased the yield of ammonia when DBU initial concentrations ranged from 1 mM to 10 mM. For example, addition of IPA with IPA/DBU ratios of 1 (5 mM of each) significantly decreased the yield of ammonia by 25%. Also, there was no clear reduction in the yield of nitrate when IPA used, where a higher range of operating conditions or higher ratios of IPA probably are needed to make a clear conclusion.

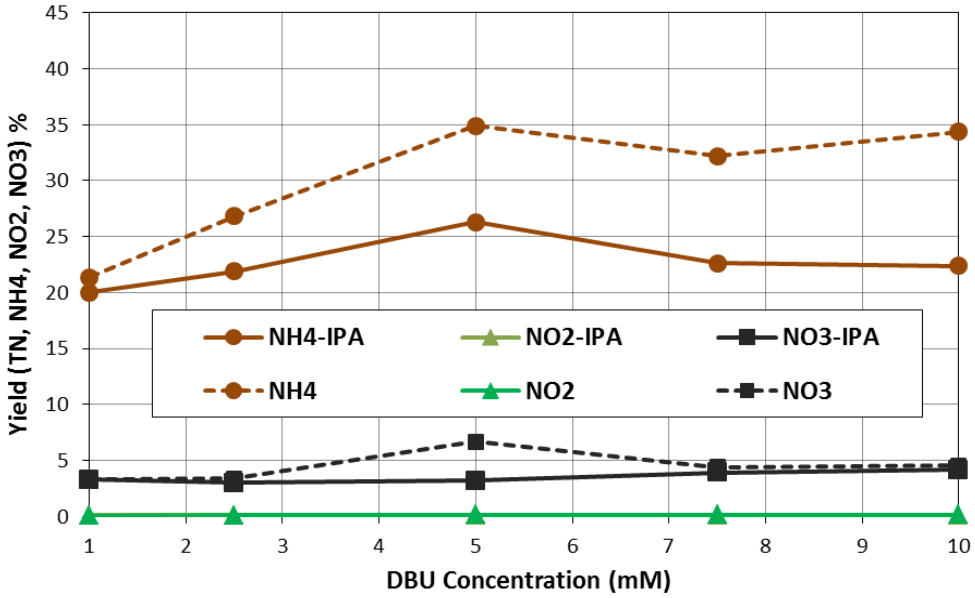


Figure 53: Nitrogen-Speciation yields as a function of DBU concentration at 400°C, with and w/o IPA, SR of 1, 250 bar and 6 s.

Figure 54 shows a summary of the effect of different DBU feed concentrations on the removal of TOC and TN and the yield of ammonia in the presence and absence of IPA. It shows how the presence of IPA improved TN removal for the whole range of DBU concentrations studied. For example, the TN removal enhanced by around 10% with 2.5 mM DBU and by 4%

with 10 mM of DBU when stoichiometric IPA added. Also, maximum TN removal of 94% was achieved with 10 mM of DBU when IPA used. TN removal was slightly lower than that of TOC due to the complexity of nitrogen chemistry where relatively higher temperatures are needed to eliminate nitrogen. On the other hand, the yield of ammonia decreased significantly with all DBU concentrations studied when IPA was supplied, as discussed in Figure 53. Combining these results showed that presence of IPA shifted the reaction more towards gases phase as to N_2 and CO_2 even though only 400^{o}C and stoichiometric IPA was used here.

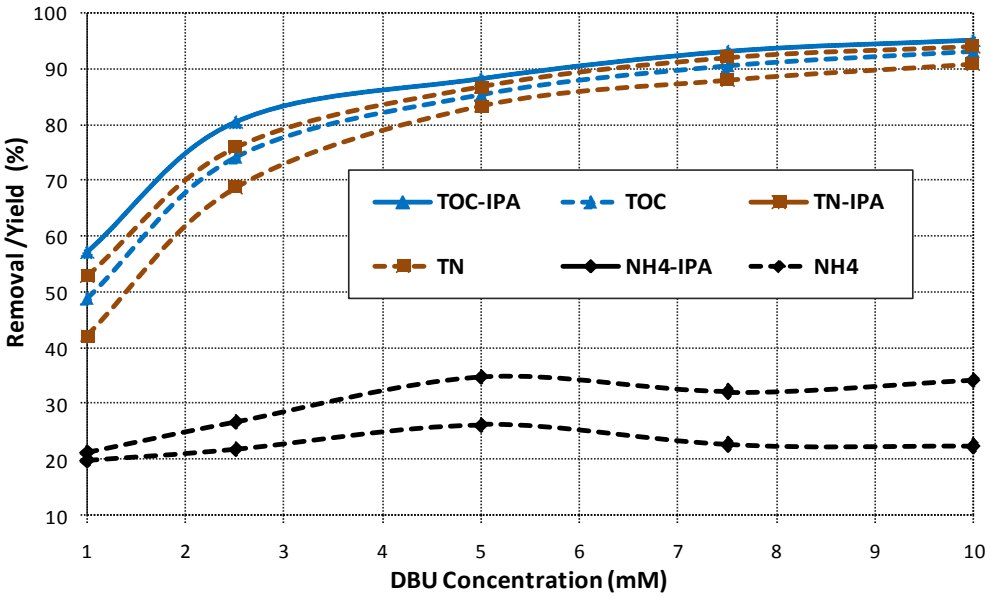


Figure 54: Effect of DBU concentration on TOC, TN removals and NH_4 yield with and without IPA at 400^{o}C, SR of 1, 250 bar and 6 s.

6.4.5 Effect of Oxidant Ratio

Figure 55 shows the effect of oxidant on the TOC removal of DBU as oxidant ratio increased from 0.8SR to 2SR (100% excess) in the presence of IPA, compared to the same levels of oxidant in the absence of IPA. The positive effect of oxidant in the absence of IPA was discussed in Section (5.3.5). In general the graph shows an enhancement in the role of oxidant in the presence of IPA with all oxidant ratios studied. For example, with lower oxidant ratios like 0.8 SR and 1.25 SR, IPA also enhanced the TOC removal by 5% and 2% at 2 and 10 seconds, respectively. Also, with 2 SR (100% excess), adding IPA improved the TOC removal by 2% at 10 seconds of residence time. The best TOC removal of 95.1% was obtained with 2SR when IPA added. This promising improvement in the removal of TOC with oxidant was at a mild temperature of 400°C and using only IPA/DBU ratio of 1. Therefore, using higher IPA ratios with this range of oxidant would achieve a better destruction rather than elevating the operating temperatures. During investigating oxidant, residence time showed also a positive effect on TOC destruction. For example, with all oxidant ratios investigated, residence time made an improvement of around 3% on TOC removal when increased from 2 to 10 seconds.

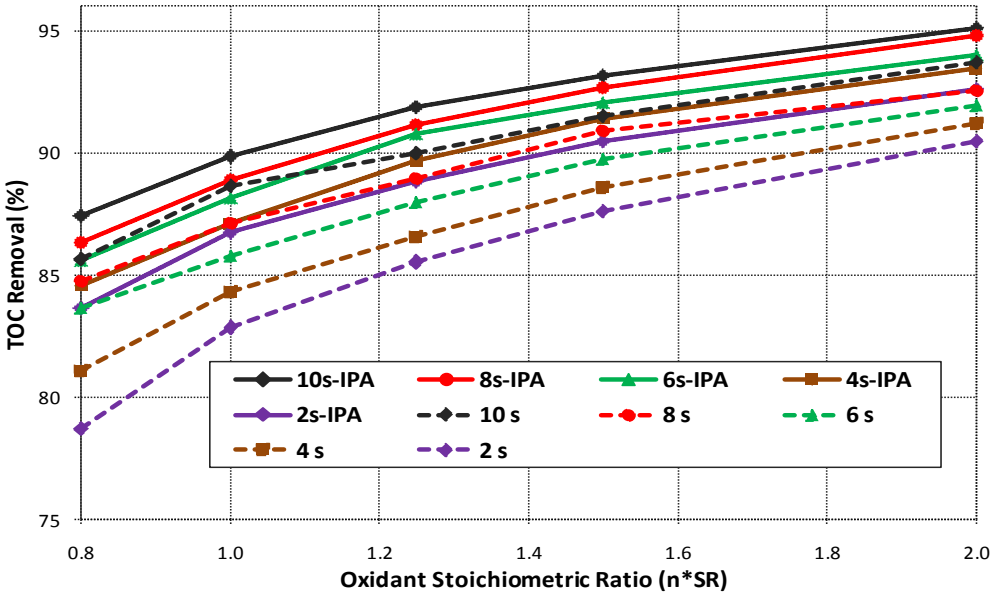


Figure 55: Effect of oxidant stoichiometric ratio on TOC removal at 400°C, 5 mM DBU, with and w/o IPA, 250 bar and various residence times.

Figure 56 illustrates obviously the effect of oxygen on the yield of nitrogen products, where first increasing oxidant ratios decreased unwanted ammonia and other species in liquid phase as a good sign of destruction. Then, the presence of co-fuel showed a significant effect to decrease the yield of nitrogenous species with all oxidant ratios investigated. For example, at 6 seconds of residence time adding IPA decreased the yield of ammonia by 25% and 20% with 1SR and 2SR, respectively. Nitrate also decreased with all oxidant ratios when IPA added, while nitrite was at its lowest level. The reduction in nitrogenous species indicated that more nitrogen was converted to the gaseous phase when IPA was used, which is a good sign of destruction. The presence of IPA enhanced the role of oxidant through providing more free radicals to the system during IPA oxidation.

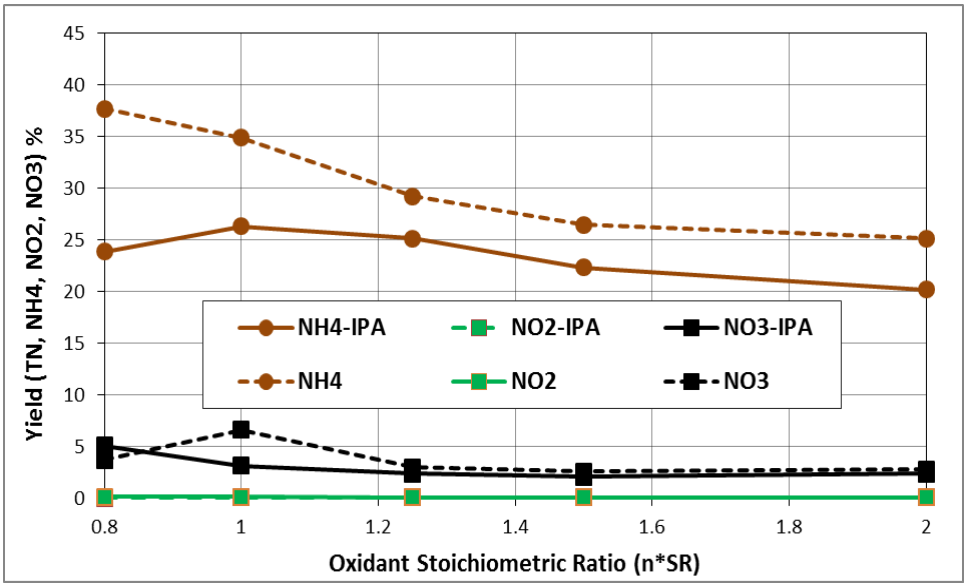


Figure 56: Nitrogen-Speciation yields as a function of oxidant stoichiometric ratio at 400°C, 5 mM DBU, with and w/o IPA, 250 bar and 6 s.

Figure 57 shows a general view of the removals and the yield of ammonia with varying oxidant amounts. Besides the positive influence of oxidant to reduce ammonia yield and improving TOC and TN removals, the presence of IPA improved TN removal with all oxidant ratios studied. For example, the TN removal increased by around 7% with 0.8 SR and by around 4% with 2SR when IPA added. A maximum TN removal of 93.2% was achieved with 2 SR when IPA was used. Also, the presence of IPA with all oxidant levels enhanced the TOC removal and reduced ammonia yield as previously discussed in Figures 55 and 56. Combining these results showed that presence of IPA shifted the reaction more towards final gaseous products as to N_2 and CO_2.

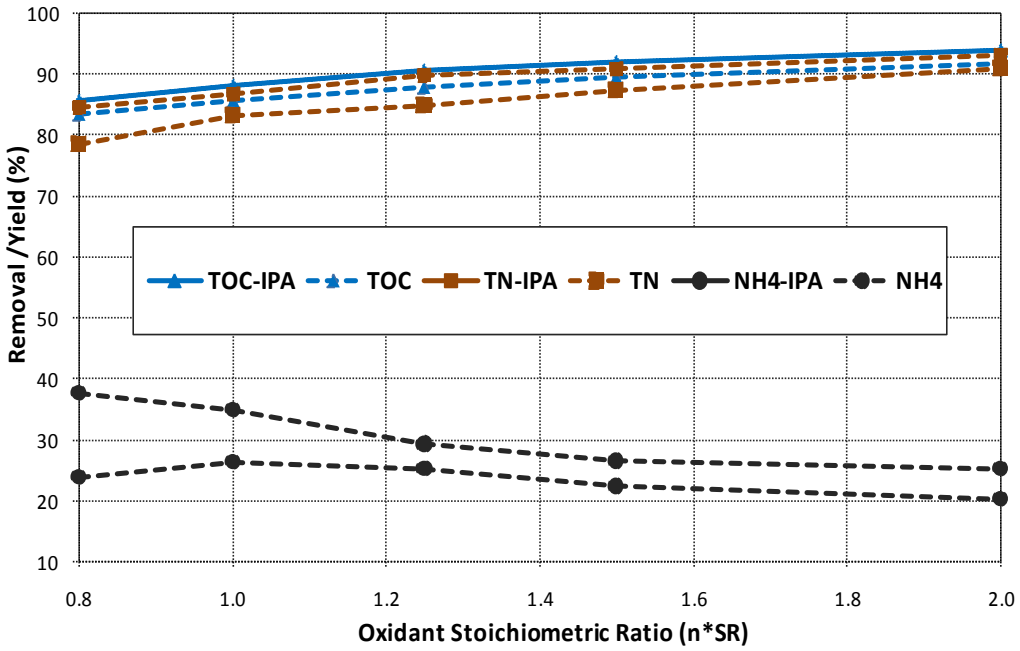


Figure 57: Effect of oxidant stoichiometric ratio on TOC, TN removals and NH_4 yield with and without IPA at 400°C, 5 mM DBU, 250 bar and 6 s.

6.4.6 Effect of IPA Concentration Ratio

Figure 58 shows the effect of different ratios of IPA concentration on the TOC removal. It showed that adding IPA significantly enhanced the TOC removal and thus DBU destruction. First, the absence of IPA achieved a minimum TOC removal of 87.4% at 10 seconds of residence time. Then, addition of IPA showed a significant ability to enhance the TOC removal with all IPA ratios investigated. For examples, the TOC removal steadily improved by around 5% when IPA/DBU ratio ranged from 1 to 4. This general trend agrees with previous works that showed the presence of organics (as alcohols) positively improved the TOC conversion. For instance, it has been found that the presence of IPA as an auxiliary fuel positively enhanced the TOC removal (Cocero et al., 2000a, Bermejo et al., 2008). Also, a similar observation was reported with ethanol during methylphosphonic acid oxidation (Ploeger et al., 2006b). In this work,

maximum TOC removal obtained was 93.6% with IPA/DBU ratio of 4, which is promising as this set of the work was carried out with a mild temperature of 400°C and supplying only 1SR of oxidant. Thus, using higher IPA/DBU ratios would significantly enhance the removal without the need for using higher temperatures. Moreover, the trend of TOC removal here show that it is still expected that higher ratios than 4 or even higher than 6 could help to improve the destruction further.

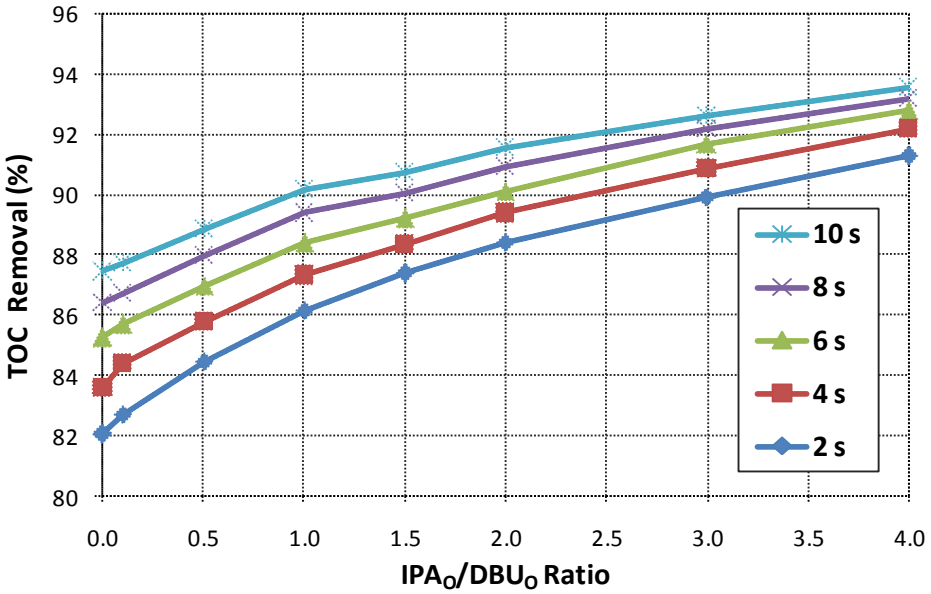


Figure 58: Effect of IPA/DBU ratio on TOC removal at 400°C, 5 mM DBU, 1 SR, 250 bar and various residence times.

Figure 59 shows the yield of nitrogenous species with varying IPA amounts. The presence of IPA compared to the non-IPA system showed the positive effect of IPA on nitrogen pathway. For example, the yield of ammonia decreased by 11% when IPA added with just a ratio of 0.1 compared to non-IPA system. Then, the presence of IPA with the rest of IPA/DBU ratios used (from 0.1 to 4) considerably decreased the yield of nitrogenous species. For example, the yield of ammonia and nitrate decreased by around 40% when IPA/DBU ratio increased from 0.1 to 4 (20

mM IPA/5 mM DBU). Also, their yields decreased by 23% as IPA/DBU ratio increased from 1 to 4. This indicated that more IPA would convert more organic nitrogen (in the feed) to nitrogen gas as a sign of further destruction. It seems that higher ratios of IPA would enhance the reduction of ammonia further. Oe and co-workers reported that the presence of alcohols strongly affected nitrogen behaviour during co-oxidation (Oe et al., 2007).

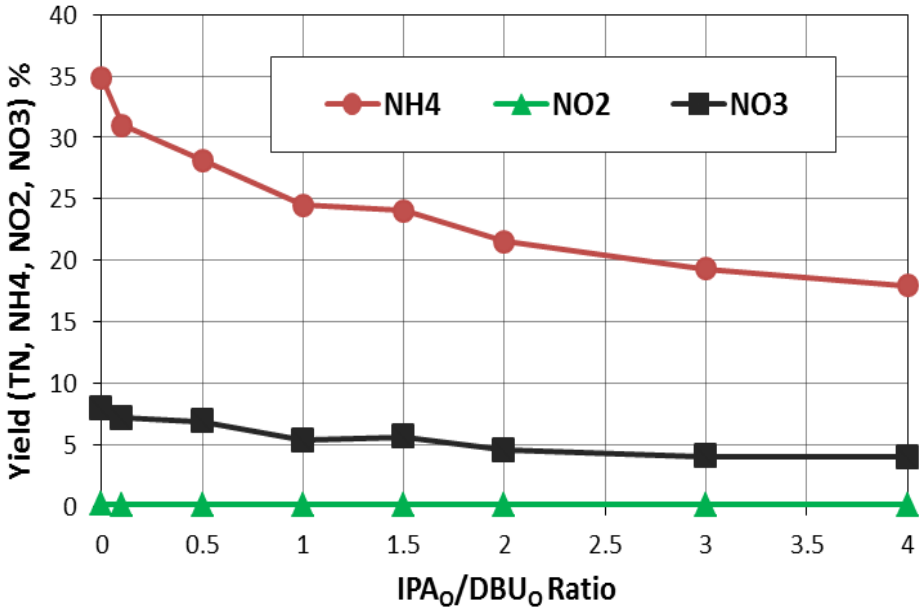


Figure 59: Nitrogen-Speciation yields as a function of IPA/DBU ratio at 400^{o}C, 5 mM DBU, 1 SR, 250 bar and 6 s.

A summary of removals and the yield of ammonia with varying IPA amounts is shown in Figure 60. As previously discussed the presence of IPA up to a ratio of 4, clearly enhanced TOC removal and decreased the yield of ammonia. Also, here the presence of IPA enhanced TN removal with all IPA/DBU ratios and exactly in the same manner of TOC removal indicating that co-fuel oxidizes Carbon and Nitrogen similarly. Cabeza and co-workers observed a similar trend where IPA improved TN removal during ammonia oxidation under similar conditions (Cabeza et

al., 2014). The combination of these results shows that the addition of more IPA forced the reaction more towards final gaseous products as to N_2 and CO_2.

The positive role of IPA in enhancing the destruction efficiency during DBU co-oxidation can be explained based on the reported suggestions by several authors. For instance, the presence of IPA (as auxiliary fuel) increases the enthalpy content of the feed mixture where excess heat is generated during oxidation reaction and ultimately a better removal is obtained (Bermejo et al., 2008). It was found that a 1 wt% and 5 wt% IPA gave temperature of 400^{o}C and 708^{o}C with a TOC removal ranged from 62% to 99.7% (Cabeza et al., 2011). Also, this reduces the operating temperatures for organic removal. Another suggestion is that IPA generates reactive radicals (OH) that effectively enhance the oxidation (Helling and Tester, 1988, Ploeger et al., 2006b, Cabeza et al., 2014). Finally, alcohols are easily oxidised compounds, in which their presence accelerates other organics oxidation rate (Killilea et al., 1992, Ploeger et al., 2007).

Moreover, adding organics with high-energy value as in the case of IPA would provide the right enthalpy content for the feed stream that enables to preheat the feed (self-sufficient operation) when this energy is recovered or to produce electricity, which ultimately improves the process economics (Cocero et al., 2000a, Queiroz et al., 2015).

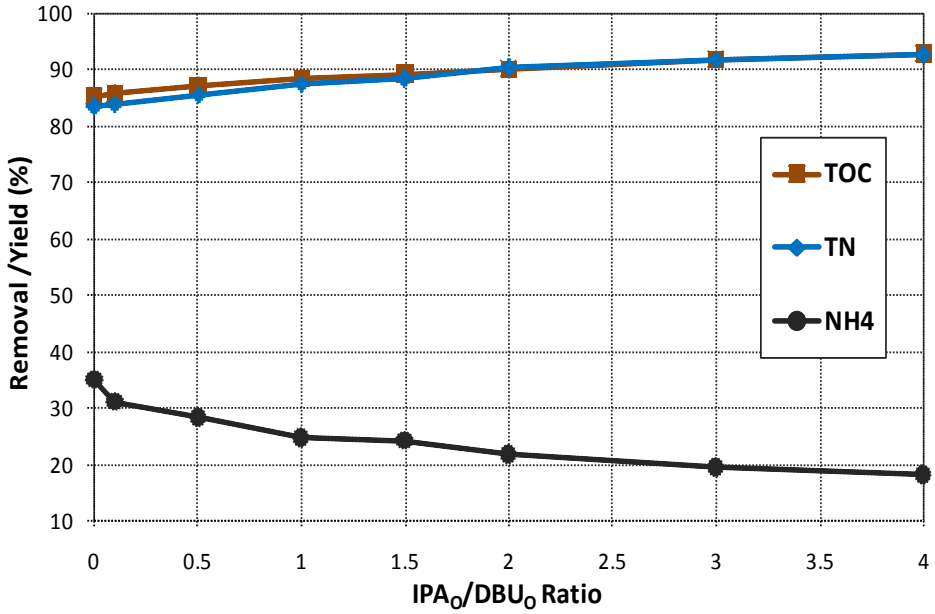


Figure 60: Effect IPA/DBU ratio on TOC, TN removals and NH_4 yield at 400°C, 5 mM DBU, 1 SR, 250 bar and 6 s.

6.5 Summary

Results showed the positive effect of adding IPA during the SCWO of DBU comparing to the preliminary results obtained from investigating ranges of temperatures, organic initial concentrations, oxidant ratios and residence times. The presence of IPA obviously improved the oxidation of DBU through the removal of TOC and TN. Moreover, adding IPA showed ability to decrease the yield of ammonia as an unwanted intermediate either with other variables or when different IPA/DBU ratios were studied independently. Co-fuel also can decrease the needed operating temperature that would improve the SCWO system economics. Moreover, this would minimize the needed temperature that required for ammonia removal. In future, deep investigation is needed to determine the optimized milder operating conditions for removal of the starting material and intermediate ammonia especially in the presence of IPA.

6.6 Global Kinetics of DBU Oxidation in Presence of IPA

Details and steps of kinetics analysis of DBU oxidation are explained in Chapter 5, Section 5.5. In this part, the same procedure was followed for the kinetics of SCWO of DBU oxidation in the presence of IPA. The qualitative investigation of the effects of different process variables as temperature, organic concentration, oxidant ratio and residence time on the kinetics of DBU decomposition in the presence of IPA was performed as previously illustrated in Section 6.4.

To study quantitatively the effects of these parameters, kinetic analysis was conducted to find reaction rate parameters, namely the reaction rate constant (k), the Arrhenius parameters, namely the pre-exponential factor (A), activation energy (Ea) and the orders of reaction with respect to DBU (a), oxidant (b) and water (c) using global power-rate law expression. The SCWO kinetic model has been developed from the global rate law expression as in equation (6.4) below:

$$\frac{-d[Organic]}{dt} = k[organic]^a[oxidant]^b[H_2O]^c = A\exp^{\left(-\frac{Ea}{RT}\right)}\ [organic]^a[oxidant]^b[H_2O]^c \quad (6.4)$$

Where, the terms of this equation are explained in Section 5.5.

In this part, the kinetic analysis was performed by fitting the obtained experimental data to the global power law by two steps:

- Pseudo –first-order approximation

- Integral method approximation

Water as a reaction medium for the SCWO of DBU and IPA was always represents more than 99% of medium (in excess), therefore the concentration of water was considered constant that has no effect on the DBU oxidation rate. Thus, reaction order with respect to water is zero.

6.6.1 Pseudo-First-Order Approximation

The global kinetics for SCWO of organic wastewaters have been described by several researchers by pseudo-first-order expression, that expresses a reaction of order of unity with respect to the organic and zero with respect to oxygen (Helling and Tester, 1988, Pinto et al., 2006b, Abelleira et al., 2013). This is a good initial simplification as the oxygen used in all runs was always in excess to ensure completely oxidising DBU and IPA. This makes the global power-rate law expression as follows:

$$rate = \frac{-d[DBU]}{dt} = k[DBU] \quad (6.5)$$

And since TOC values are the experimental conversion data, the equation was modified to be:

$$rate = \frac{-d[TOC_{DBU}]}{dt} = \mathrm{k}[\mathrm{TOC}_{DBU}] \quad (6.6)$$

By integrating equation 6.6 gives equation (6.7) at any given temperature;

$$\ln\left(\frac{[\mathrm{TOC}]}{[\mathrm{TOCo}]}\right) = -Kt \quad (6.7)$$

Ln ([TOC]/[TOC_o]) can then be plotted against time (t) for each temperature to obtain *k* from the slop. Figure 61 illustrates this.

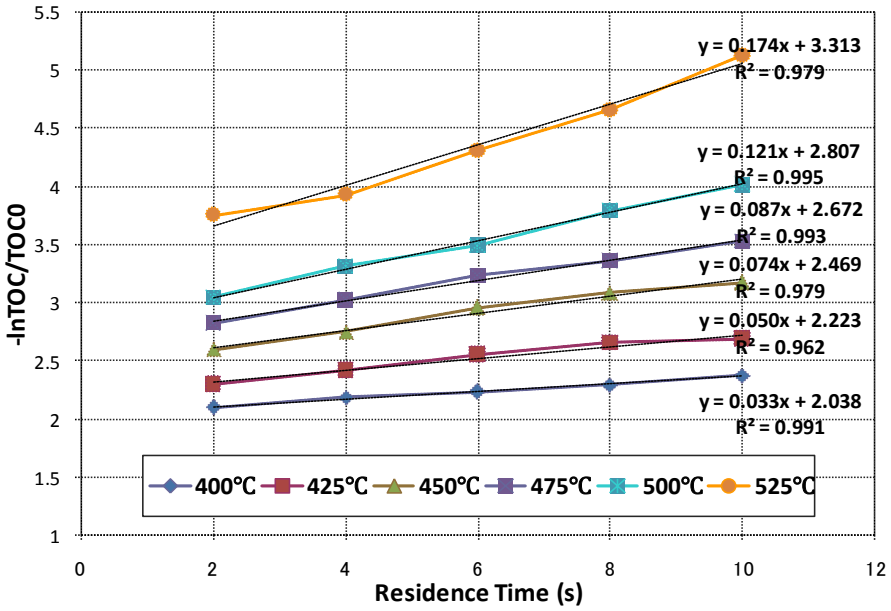


Figure 61: Natural logarithm of (TOC/TOC_o) versus residence time for DBU co-oxidation experiments at studied temperatures and a pressure of 250 bar.

In order to determine Arrhenius parameters as activation energy (*Ea*) and pre-exponential factor (*A*), the natural logarithm of obtained rate constant (*k*) for each temperature was plotted versus temperature inverse (1/T) as shown in Figure 62.

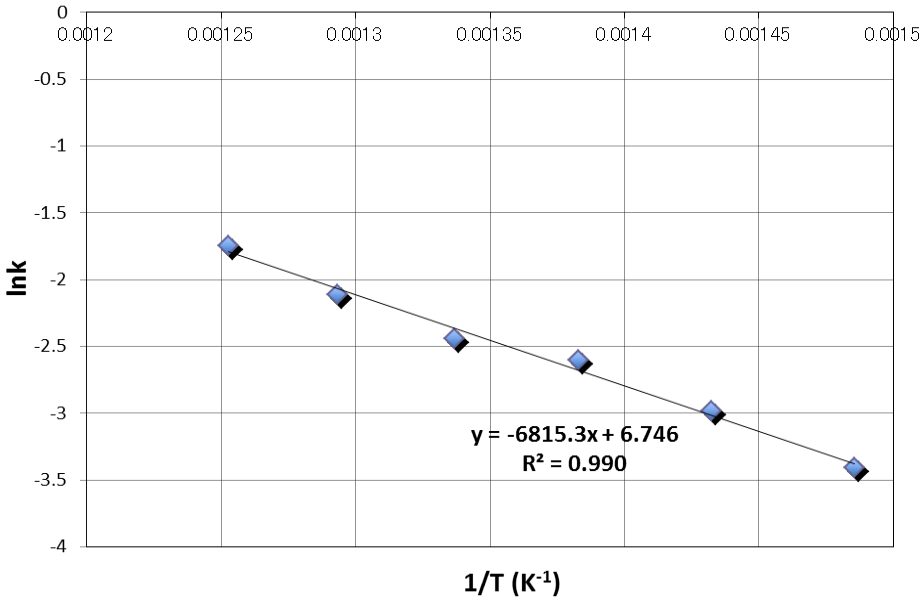


Figure 62: Arrhenius plot for the oxidation of DBU and IPA.

Therefore, the value of activation energy was determined by multiplying the slop (6815) by the universal gas constant (8.314 J/mol.K) that gave *Ea*=56662.4 J/mol and the value of pre-exponential factor was calculated from ln *A*= intercept, and this gave *A*=851.4 s^{-1}. Therefore, the emerged Pseudo-first-order rate expression for the oxidation of DBU and IPA at the temperatures investigated is given by:

$$rate = \frac{-d[TOC_{DBU}]}{dt} = 851.4\ (s^{-1})\ exp\left(-\frac{56662\ J/mol}{RT}\right)[TOC_{DBU}] \qquad (6.8)$$

There was a little effect of IPA on the activation energy of DBU co-oxidation in this part, which is probably due to a minor analytical error.

6.6.2 Integral method approximation

To understand more the development of the global rate expression for DBU co-oxidation, integral method approximation was used to mathematically express the kinetic data. To determine the global kinetic parameters for DBU co-oxidation, equation (6.4) was used by considering that the order of organics (DBU+IPA) equal to one. These parameters were regressed from the complete set of data to predict the reaction rate of BDU destruction over the conditions investigated and by assuming that the co-oxidation of DBU is only a function of temperature, DBU and oxygen concentrations as water was always in excess amount (>99% water). Although several works of oxidation kinetics in SCWO suggested that the oxygen order is zero (as previously discussed), it is worth discovering any influence of oxygen concentration on the DBU destruction in the presence of IPA. Therefore, oxidant effect experiments were carried out at 400^{o}C, 5 mM DBU, 5 mM IPA, 250 bar and with five oxidant ratios (from 0.8 SR to 2 SR) that represent from 70 mM to 175 mM oxidant concentration at reactor inlet. The TOC removal for these experiments was shown in Figure 55 in Section 6.4.5. It showed obviously an increase in

the TOC removal as oxygen concentration increased. Thus, the order of reaction with respect to oxygen should be higher than zero and then the previous assumption (Pseudo-first order approximation) for DBU co-oxidation needs to be improved. Therefore, PFR design equation was used to determine the order of oxygen using integral method approximation with a=1 and b > zero where equation 6.4 can be rearranged as below:

$$(-rA) = \frac{-d[DBU]}{dt} = k[DBU][O_2]^b = A\,exp^{\left(-\frac{Ea}{RT}\right)}\,[DBU][O2]^b \qquad (6.9)$$

The concentration of oxidant can be assumed constant ($[O_2]=[O_2]_o$). The performance equation for steady-state plug flow reactor was applied (Levenspiel, 1999) as follows:

$$\frac{\tau}{[DBU]_O} = \int_0^X \frac{dX_{DBU}}{(-rA)} \qquad (6.10)$$

Where $\boldsymbol{\tau}$ is the residence time, $[DBU]_o$ is the DBU initial concentration, X_A is the conversion of DBU and $(-r_A)$ is the reaction rate for the SCWO of DBU.

Substituting equation 6.9 into equation 6.10 yielded the following equation:

$$\ln\left(\frac{1}{(1-X_{DBU})}\right) = k.t[O_2]_o^b \qquad (6.11)$$

Thus, to determine the numerical estimate of b value, it is essential to plot ln[1/(1-X)] versus $\boldsymbol{\tau}$ for oxygen concentration experiments. Then, the slopes of all straight lines produced $k[O_2]_o^b$ as shown in Figure 63.

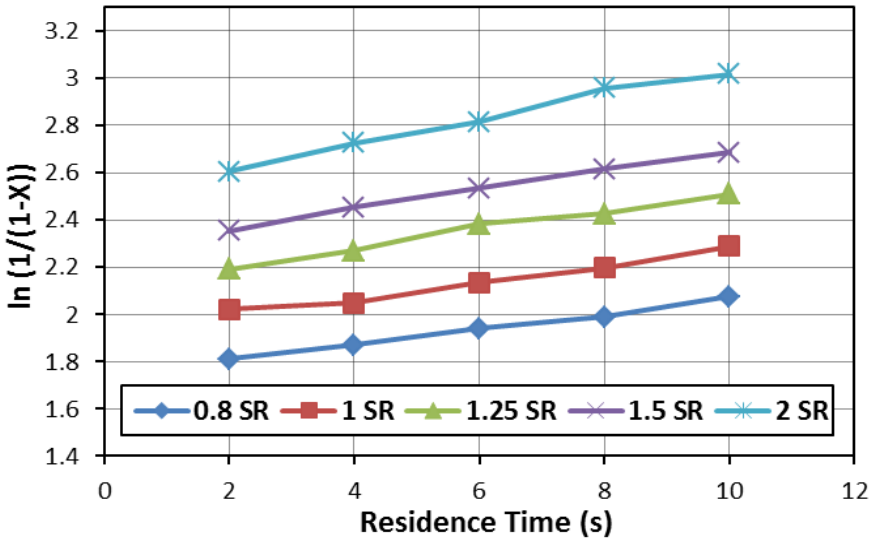


Figure 63: Natural logarithm of (1/(1-X)) versus residence time for DBU co-oxidation experiments with varying oxidant concentrations.

By taking the natural logarithm of $k[O2]_o^b$, this term can be written as:

$$\ln(k[O_2]_o^b)=\ln(k)+b\ln([O_2]_o) \quad (6.12)$$

Therefore, plotting these slopes ($k[O_2]_o^b$) from Figure 63 as a function of the oxygen concentration on a logarithmic scale will produce a straight line with a gradient of *b* as shown in Figure 64.

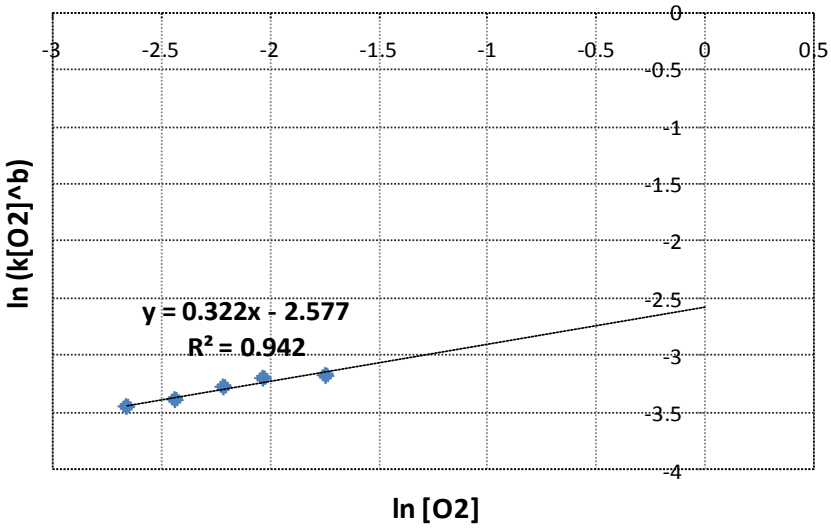


Figure 64: Determination of oxygen reaction order.

The slope of the straight line was 0.32 which is the order of reaction with respect to oxygen. By determination of the reaction orders for the global rate law for DBU and oxygen as (a=1 and b=0.32), to determine the values of k previous equation (6.11) was simplified to:

$$k = ln\frac{1}{(1-X_{BDU})} \times \frac{1}{\tau} \times \frac{1}{[O2]^{0.32}} \qquad (6.13)$$

Then, the values of reaction rate constants were calculated using conversion data for different temperature effects where as expected the increase in reaction temperature resulted in higher rate constant. Then, to find the values of *Ea* and *A* for the new *ki* values, Arrhenius plot for the natural logarithm of *k* versus 1/T was plotted as shown Figure 65. *Ea* and *A* were determined to be 21965.6 J/mol and 41.06 $M^{-0.32}$ s^{-1}, respectively.

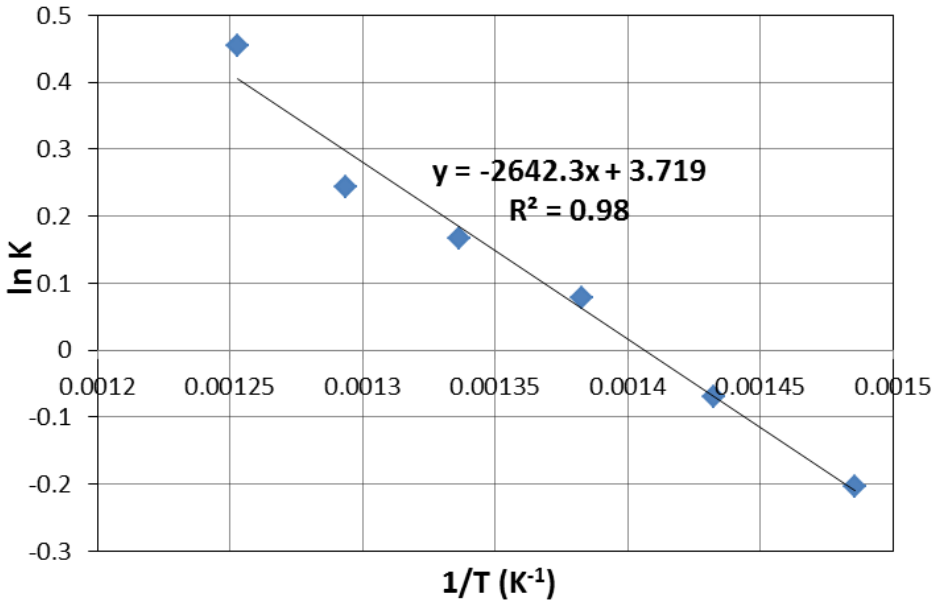


Figure 65: Arrhenius plot for DBU oxidation, P=250 bar.

Thus, the generated global rate expression for the destruction of DBU up to a temperature of 525°C is as follows:

$$rate = \frac{-d[TOC_{DBU}]}{dt} = 41.06\ (M^{-0.32}\ s^{-1})\ exp^{\left(-\frac{21965.6\frac{J}{mol}}{RT}\right)}[TOC_{DBU}]\ [O2]^{0.32} \qquad (6.14)$$

6.7 Summary

Kinetic analysis of DBU co-oxidation showed that IPA addition effectively decreased the activation energy of the reaction (decreased from 25.7 to 21.9 kJ/mol), thus a faster reaction rate could be obtained. Using an integral approximation was suitable to describe the kinetics of DBU, where the oxidant was found to have an influence on DBU decomposition with an order of 0.32. This matches another work that found oxygen had an order of 0.4±0.1 during DBU hydrothermal decomposition (Al-Duri et al., 2008). Also, the given extra heat by IPA would allow for working under milder conditions during the removal of starting material or the elimination of ammonia as unwanted by-product.

CHAPTER 7- ENHANCEMENT OF AMMONIA REMOVAL IN SUPERCRITICAL WATER OXDIATION USING ISOPROPYL ALCOHOL (IPA)

7.1 Introduction

This chapter illustrates the results and their discussion for the experiments that were performed to study the supercritical water oxidation of ammonia as a starting material. The aim of this work is to specifically investigate the removal of ammonia using Isopropyl alcohol (IPA) as enhancer, compared to IPA-free system. Previous works showed that ammonia is the most refractory nitrogen-containing compound where higher temperatures, longer residence times or catalyst or a mixture of all is needed (Ding et al., 1998, Ploeger et al., 2007). Some review studies have pointed out that ammonia removal could be improved in the presence of other organic compounds, such as easily oxidised alcohols (Killilea et al., 1992, Cocero et al., 2000a). However, there were some contradicting results regarding the ammonia removal obtained with co-fuels as some achieved complete removal while others obtained low removals in addition to the effective co-fuel ratios (Bermejo et al., 2008, Cabeza et al., 2014). This might be due to using different operating conditions, reactor systems, and co-fuels. This chapter deals with studying the SCWO of ammonia first as a preliminary study in the absence of co-fuel, followed by using IPA as a promising co-fuel with a wide range of IPA/ammonia concentration ratios. This was also associated with investigating the effects of the typical operating conditions on the system, such as temperature, oxidant ratio and residence time. It is also anticipated that adding co-fuel would reduce the severe operating conditions that are normally needed for ammonia removal. The main

parameters used were total nitrogen removal (%TN removal), ammonia removal (%NH_4-N removal) and nitrogen conversions into nitrite and nitrate.

7.2 Ammonia Selection

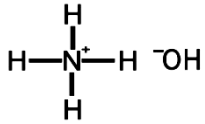
Ammonia consists of nitrogen and hydrogen and is known as the simplest refractory compound. It is chemically stable even it has a simple structure. This recalcitrant nature is due to the existence of nitrogen atom that forms strong triple bonds and thus, there is a lot of energy in nitrogenous compounds as the triple bond is hard to break due to a high energy value. At room temperature and pressure ammonia appears as a colourless gas and its chemical formula is NH_3. In nature, Ammonia solution also known as ammonium hydroxide (NH_4-OH) is a solution of ammonia (NH_3) dissolved in water. It can be also abbreviated by the symbols NH_3 (aq).

Ammonia has many applications as a raw material for the production of various compounds. For example, ammonia compounds are used as fertilizers. Ammonia is also the basic unit in the production of many pharmaceuticals. For household uses, dilute ammonium hydroxide is used as a cleaning agent. Naturally, plants need ammonia in the soil to make nutrients. Liquefied ammonia has been widely used as a refrigerant. Moreover, it used in the synthesis of Nylon and the cleaning of silk, cotton and wool. Dilute ammonia solutions are used as a source of nitrogen in fermentation industry. Also, ammonium hydroxide is used to darken wood in furniture industry. Ammonia is used as antimicrobial agent in food production. Also, it is used to neutralise nitrogen oxides (NO_x) pollutants, and has been proposed as alternative to fossil fuel for internal combustion engines. Ammonia is the precursor to numerous nitrogen-containing compounds. For example, Amines can be produced by reacting alkyl halides with ammonia and amides formed by reacting ammonia with carboxylic acid derivatives. Nitric acid is an important derivative as it is

used for the production of fertilizers, explosives, and many organo-nitrogen compounds. Compounds as Hydrogen cyanide, Phenol, urea, ammonium carbonate and amino acids are produced from ammonia. In industry, ammonium hydroxide is used as a precursor to alkyl amines, hexamethylenetetramine and ethylenediamine.

The physical properties of ammonia solution, ammonium hydroxide (Fisher Scientific, UK, 35% in mass) used in this study are illustrated in Table 17. It was a colourless liquid and showed complete miscibility in water during all runs. To overcome the strong smell of ammonia and its toxicity, strict lab handling rules were followed such as using fume cupboard, gloves and filter gas mask.

Table 17: Physical properties of ammonia solution (Chembook, 2016).

Ammonium solution , CAS number: 1336-21-6	
Structure	
Molecular formula	NH_4OH
Appearance and solubility	Colourless liquid, miscible with water
Molar mass	35.04 g/mole
Density	SG 0.880 g/ml at 20^oC
Boiling point	24.7^oC
Melting point	-91^oC

The reasons behind selecting ammonia in this study are listed below:

- Ammonia is hazardous and the most refractory compound that is widely used in pharmaceutical and several wastewater sources. Therefore the SCWO investigation of ammonia is highly interesting.

- This study also would help to know more about the SCWO of wide classes of nitrogen containing compound as conducted in this thesis, starting from DMF, DBU and lastly ammonia.
- Previous studies on co-oxidation of ammonia using co-fuels showed some contradicting results regarding ammonia removals obtained and the effective ratios of co-fuel/ammonia. These contradictions might be due to using different system designs, conditions and co-fuels. Therefore, there is still a need for further studies to investigate the co-oxidation of ammonia using a co-fuel, namely IPA as a novel approach in this study in order to investigate its effect on ammonia removal and effective molar ratios of IPA/ammonia. Moreover, the study will investigate co-fuel ability to minimise the operating temperature as it has been reported that ammonia requires at least 650^{o}C for complete removal (Webley et al., 1991).

7.3 IPA Selection

Details about Isopropyl alcohol (IPA) and its uses, physical properties and the reasons of selection were previously explained in Section 4.3.

Part 1: SCWO of Ammonia (Preliminary study)

7.4 Effect of System Operating Conditions

7.4.1 Experimental Work Plan

In this part, the SCWO of ammonia in solutions with water was carried out at varying operating temperatures, oxidant stoichiometric ratios and residence times. During investigating each variable individually, a temperature of 450^{o}C, 10 mM of ammonia solution and delivering

the needed stoichiometric amount of oxidant (1 SR) were used to avoid the overlapping of the effect of each variable. The maximum concentration of ammonia in all experiments was 0.45wt%, which is suitable to avoid any excess heat and to maintain flow rates within the used HLPC pump capacities and also this range within the typical concentrations that SCWO process usually treats. The operating pressure during all runs was fixed at 250 bar as it has been widely reported that it has no effect on the process efficiency in supercritical region except to maintain the system in mono-phase system (Al-Duri et al., 2008). Residence times of 2-10 seconds were selected in all runs.

The ranges of the used operating conditions during this part were summarized in Table 18. Also, the justifications for selected ranges for every individual operating variable are explained in the subsequent sections. The stoichiometric equations for the complete oxidation of ammonia in SCWO in the absence of IPA in addition to hydrogen peroxide decomposition reaction are shown below:

$$NH_4OH + \frac{3}{4}\ O_2 \rightarrow \frac{5}{2}\ H_2O + \frac{1}{2}N_2 \qquad (7.1)$$

$$H_2O_2 \rightarrow \frac{1}{2}O_2 + H_2O \qquad (7.2)$$

Table 18: Summary of the operating conditions used in SCWO of ammonia experiments in absence of IPA.

Variable	Range	Fixed conditions
Temperature	400°C - 550°C	$[ammonia]_o$ = 10 mM SR = 1SR
oxidant ratio	0.8 – 1.5 SR	Temperature = 450°C $[ammonia]_o$ = 10 mM
Residence time: 2-10 seconds for all experiments		

7.4.2 Effect of Operating Temperature

While investigating the effect of operating temperature, a range from 400 to 550^{o}C was selected with 50^{o}C increments as it was not expected to obtain a major removal with 25^{o}C increment as ammonia always requires high temperatures. Figure 66 shows the effect of temperature on nitrogen removal at a residence time of 6 seconds. It illustrates the positive improvement in the nitrogen destruction in the form of ammonia (NH_4-N) and total nitrogen (TN) removals as temperature increased. This general trend was also observed in several works (Killilea et al., 1992, Ploeger et al., 2007, Bermejo et al., 2008). As the temperature increased from 400 to 550°C, the ammonia removal improved from 31% to 57% at 6 seconds of residence time, which represents 87% of enhancement. This result agrees with another work that found a similar removal at 540^{o}C using a tubular reactor (Goto et al., 1999). Also, the TN removal enhanced with the temperature in a similar manner and by around 84% of increase. Although temperature is the most influential factor in SCWO of organic compounds, these results show the need for using higher temperatures or following another approach to completely destroy the refractory ammonia and at optimised conditions. The removal of ammonia was just higher than that of TN especially at lower temperatures as the latter in the liquid effluent consists mostly of ammonia and traces of nitrite and nitrate. Therefore, the removal of TN tells about other nitro-species formed while ammonia removal is specifically tells about the status of initial ammonia. The residence times (2-10 s) also positively affected ammonia oxidation. Several authors observed an in increase in ammonia removal with residence time reporting that most oxidation occurred below 2 seconds (Segond et al., 2002, Cabeza et al., 2011, Cabeza et al., 2014). They explained that it was due to sufficient mixing, rapid temperature increase and radical generation.

In this work, it was impossible to use higher residence times due to low flow rates and obtaining non-turbulent flow regime after 10 seconds.

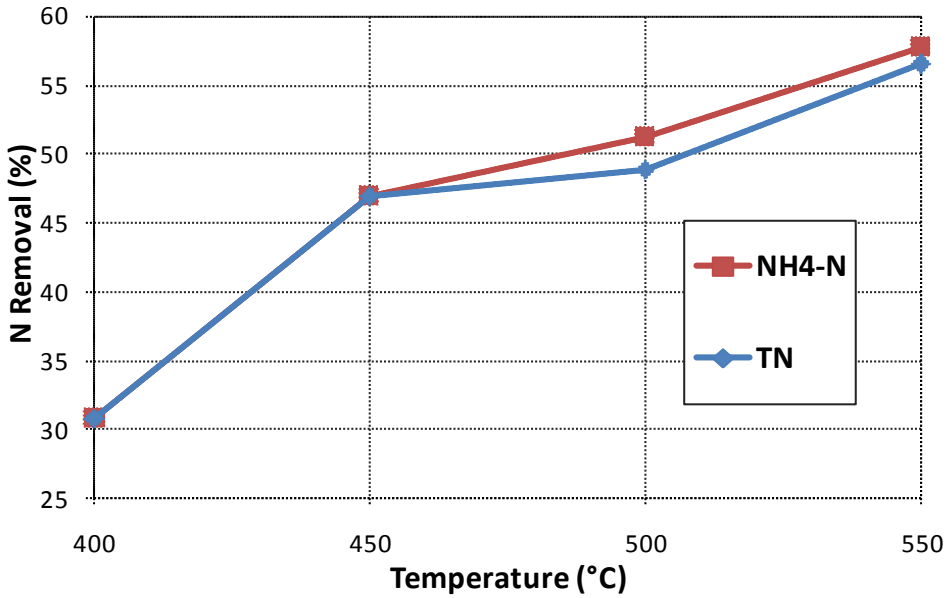


Figure 66: Effect of operating temperature on ammonia and TN removal at 10 mM ammonia, SR of 1, 250 bar and a residence time of 6 s.

Figure 67 shows the effect of temperature on nitrite and nitrate at 6 seconds residence time. It shows that increasing the temperature clearly increased the formation of nitrate as unwanted intermediate, while nitrite only appeared above 450°C. This trend for these nitrogenous species in the liquid phase was also observed in the literature (Cocero et al., 2000a, Cabeza et al., 2014). Others found nitrite levels were negligible at this range of temperature and recommended higher temperatures than those needed for ammonia to completely oxidise nitrite and nitrate (Bermejo et al., 2008, Cabeza et al., 2011). The value of nitrate concentration from this work at 550^{o}C is similar to that obtained in a previous work using a similar system (Cabeza et al., 2014).

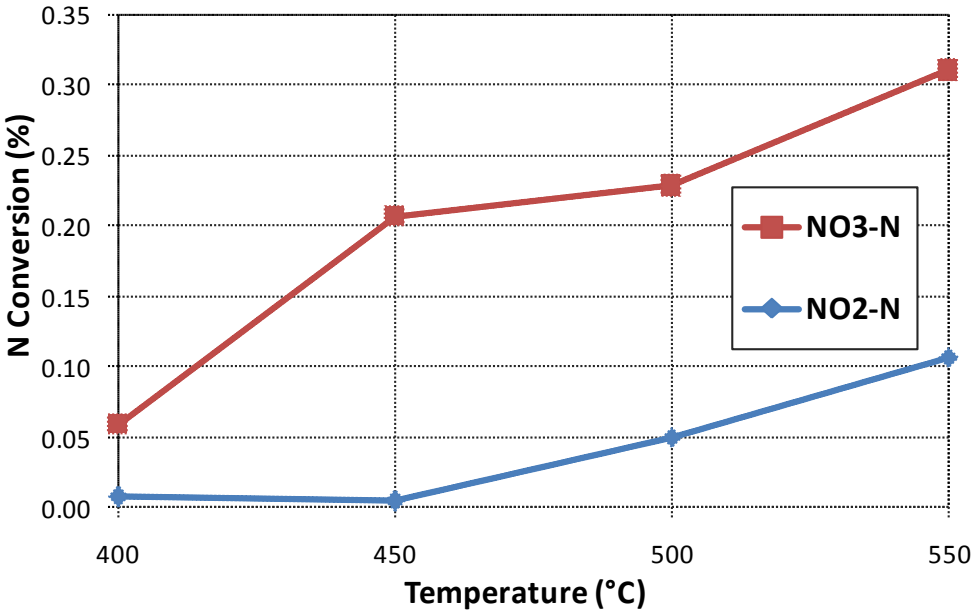


Figure 67: Effect of operating temperature on formation of nitrate and nitrite at 10 mM ammonia, SR of 1, 250 bar and a residence time of 6 s.

7.4.3 Effect of Oxidant Ratio

To investigate the effect of oxygen, oxygen dosage from 20% less than the required amount (0.8 SR) to 50% excess of oxygen (1.5 SR) was selected as it is has been reported that oxidant has no much further effect above 1.2 SR (Cocero et al., 2000b). The other operating conditions were fixed at 450^{o}C, 10 mM, 250 bars and a residence time of 2-10 seconds. Figure 68 shows the effect of oxidant stoichiometric ratio on nitrogen removal at a residence time of 6 seconds. It shows clearly the improvement in both removals of ammonia and TN as oxidant ratio increased from 0.8 SR to 1.5 SR. This general trend for ammonia destruction with oxygen was found in previous works (Ding et al., 1998, Segond et al., 2002). Results from this work showed that as oxidant ratio increased by 50% (from 1 SR to 1.5 SR) the ammonia removal improved from 38% to 57% which represents 21% of increase. Moreover, using only 25% excess of oxidant (1.25 SR) made an enhancement in the removal of ammonia by around 10%. These results are in agreement

with Ploeger's team work who found a similar ammonia removal at similar conditions (Ploeger et al., 2007). Also, the TN removal improved by around 19% at the same conditions. It can be seen that the positive influence of oxidant is still lower than that of temperature as the latter is the key influential variable to destroy ammonia. However, a combination of higher temperatures and excess of oxidant or the usage of other approaches such as using co-fuels could enhance ammonia removal. The minor variation between TN and ammonia removals indicates that a small percentage of initial nitrogen was converted to nitrite and nitrate.

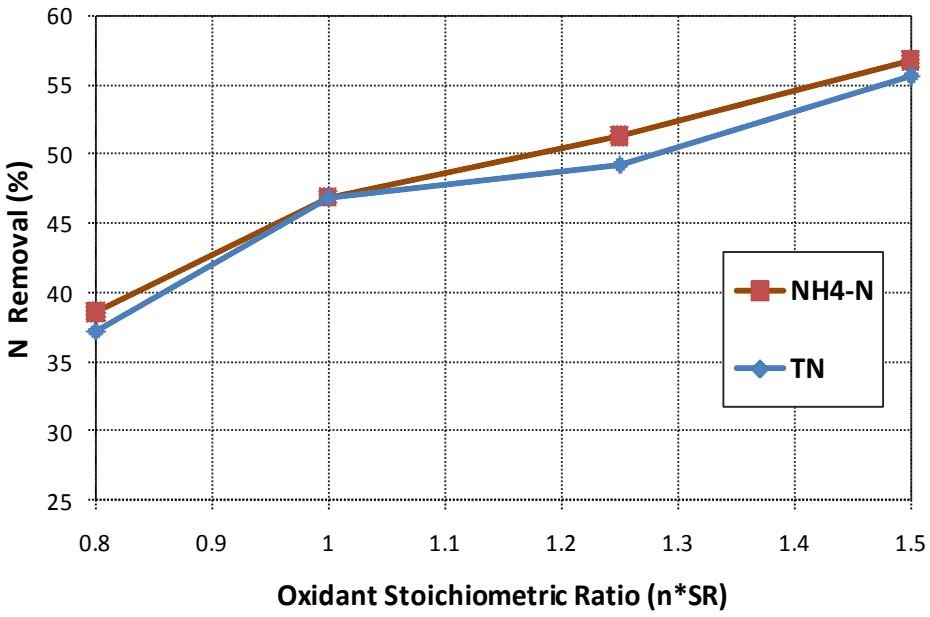


Figure 68: Effect of oxidant stoichiometric ratio on ammonia and TN removal at 400°C, 10 mM ammonia, 250 bar and a residence time of 6 s.

Figure 69 shows how oxidant ratios influenced nitrite and nitrate. Nitrate formation increased with oxidant ratio, while nitrite remained constant at minimal values as it transformed effectively into nitrate. This general trend other studies that found increasing excess oxygen increased the concentration of nitrate (Cocero et al., 2000a, Oe et al., 2007). Cabeza and co-workers also found that nitrite was always negligible in the liquid phase as oxidant increase (Cabeza et al., 2014).

They reported also the difficulty of evaluating the effect of oxygen on nitrites as the latter is unstable, therefore nitrites can be simply oxidised to nitrates at room temperature. Several researchers suggested using the stoichiometric amount of oxygen in order to achieve max ammonia destruction and to control nitrate generation (Killilea et al., 1992, Cocero et al., 2000a, Cabeza et al., 2014). The generated nitrates with more oxygen can be neutralised by adding acids, however such approach may cause plugging (Oe et al., 2007).

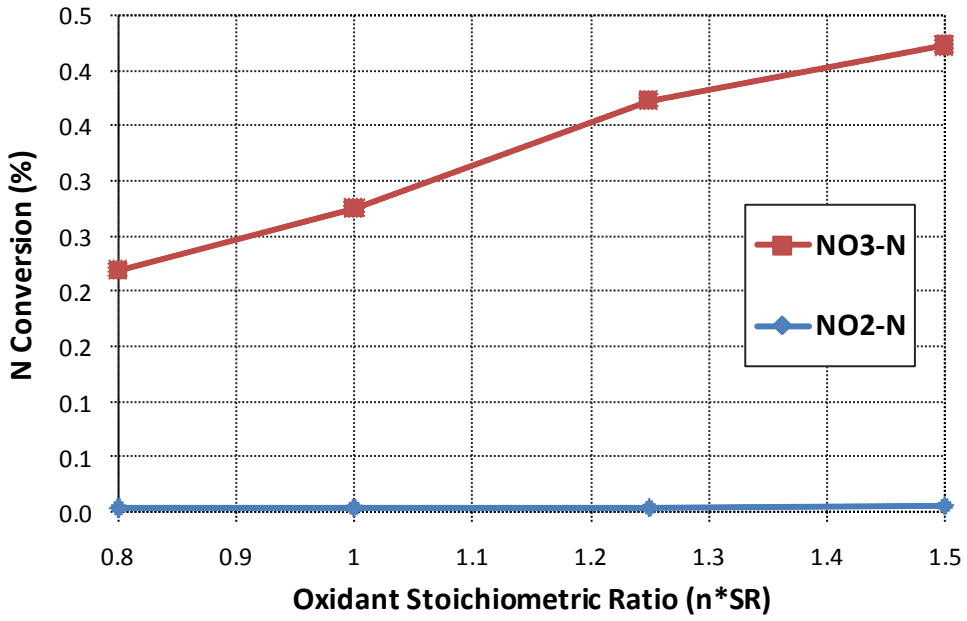


Figure 69: Effect of oxidant stoichiometric ratio on formation of nitrate and nitrite at 400°C, 10mM ammonia, 250 bar and a residence time of 6 s.

Part 2: SCWO of Ammonia in Presence of IPA.

7.5 Effect of System Operating Conditions

7.5.1 Experimental Work Plan

In this part, the SCWO of ammonia solutions in the presence of IPA was carried out at the same operating conditions that are explained in Section 7.4.1 (in part 1). During investigating IPA effect, a wide range of IPA/ammonia ratios was selected by using initial IPA concentrations of 0, 1, 2.5, 5, 10, 20 and 40 mM with 10 mM of ammonia. During investigating other variables as temperature and oxygen, 5 mM IPA was used to avoid excess heat. The maximum concentration of ammonia and IPA solutions in all experiments was 2.5wt% which is suitable to avoid any extra heat that may affect the isothermal status of the reactor and to maintain flow rates within the used HPLC pump capacities. Also, this range is suitable to be processed in the used lab-scale SCWO system without any risk of blocking and also within the typical concentration that SCWO process usually treats. The ranges of all used operating conditions during in this part are summarised in Table 19.

The stoichiometric equations for the complete oxidation of ammonia in SCWO and in the presence of IPA in addition to hydrogen peroxide decomposition reaction are shown below:

$$NH_4OH + C_3H_8O + \frac{21}{4}\ O_2 \rightarrow 3\ CO_2\ + \frac{13}{2}\ H_2O + \frac{1}{2}N_2 \quad (7.3)$$

$$NH_4OH + \frac{3}{4}\ O_2 \rightarrow \frac{5}{2}\ H_2O + \frac{1}{2}N_2 \quad (7.4)$$

$$C_3H_8O + \frac{9}{2}\ O_2 \rightarrow 4\ H_2O + \ 3CO_2 \quad (7.5)$$

$$H_2O_2\ \rightarrow \frac{1}{2}O_2 + H_2O \quad (7.6)$$

Table 19: Summary of the operating conditions used in SCWO of ammonia experiments in the presence of IPA.

Variable	Range	Fixed conditions
Temperature	400°C - 550°C	$[ammonia]_o$ = 10 mM $[IPA]_o$=5 mM SR = 1SR
oxidant ratio	0.8 – 1.5 SR	Temperature = 450°C $[IPA]_o$=5 mM $[ammonia]_o$ = 10mM
$[IPA]_o$	0-40 mM	Temperature = 450°C $[ammonia]_o$=10 mM SR= 1SR
Residence time: 2-10 seconds for all experiments		

7.5.2 Effect of Operating Temperature

Figure 70 shows the effect of temperature on nitrogen removal (NH_4-N, TN) in the presence of IPA at 6 seconds of residence time compared to IPA-free system that fully discussed in part1. Generally, the improvement in nitrogen removal was obvious with all temperatures. For example, the addition of IPA improved ammonia and TN removals by 66% at 450°C, and with 46% at 550°C even though only 50% of needed IPA was used according to the reaction stoichiometry (5 mM IPA to 10 mM ammonia). These results seemed promising compared to 65% ammonia removal that was obtained in a previous study with using ethanol at 550°C and at 2.5 seconds (Ploeger et al., 2007). This could be explained by the higher efficiency of IPA and the longer residence time (6 seconds) used in this work. Obtaining maximum ammonia removal of 84% at

550°C and in the presence of this ratio of IPA indicates that it is highly possible to achieve further removal using higher ratios of co-fuel and/or higher oxidant ratios either at the same temperature range or even at slightly higher temperatures.

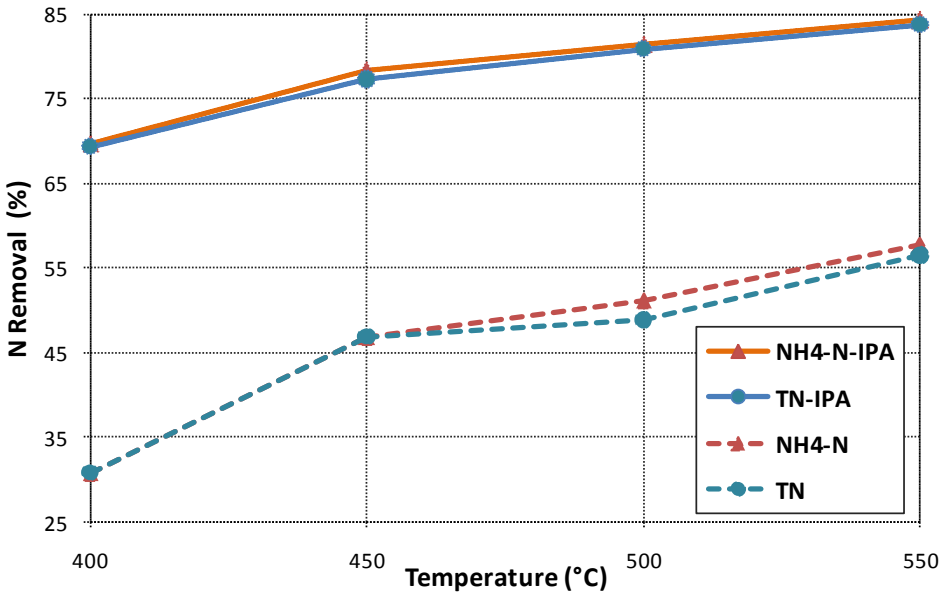


Figure 70: Effect of operating temperature on ammonia and TN removal at 10 mM ammonia, 5mM IPA, SR of 1, 250 bar and a residence time of 6s.

Figure 71 shows also the effect of varying temperatures on nitrite and nitrate in the presence of IPA compared to non-IPA system that is fully discussed earlier in this chapter. The figure shows clearly the positive role of adding IPA to reduce the levels of initial nitrogen converted to unwanted species such as nitrate and nitrite as the temperature is increased. For example, as the temperature increased from 450 to 550°C, adding IPA decreased the formation of nitrate by 35-48% and also kept nitrite at minimal levels which is a sign that IPA shifted the reaction further towards the gaseous phase. Cocero found a considerable reduction in the concentrations of nitrates and nitrites when IPA used during investigating the effect of temperature (Cocero et al., 2000a).

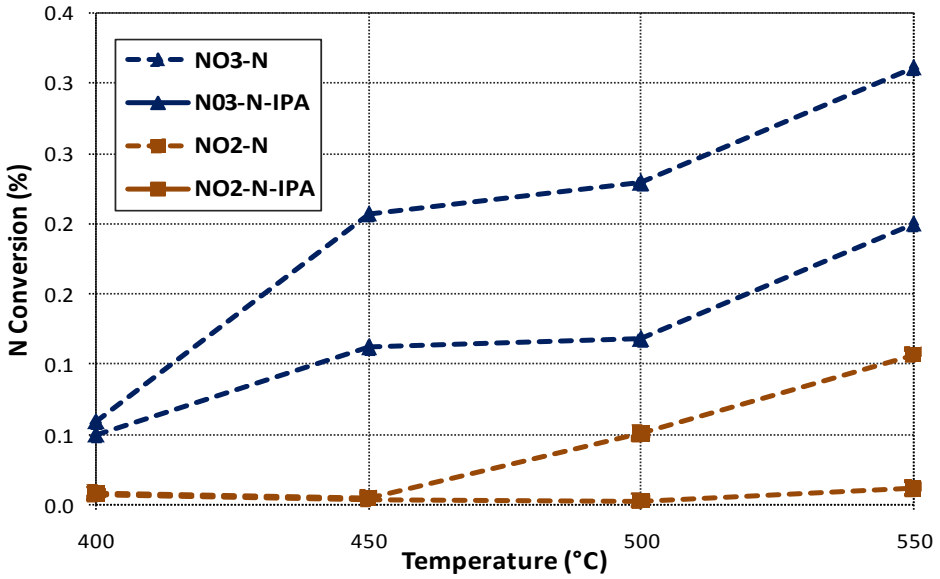


Figure 71: Effect of operating temperature on formation of nitrate and nitrite at 10 mM ammonia, 5 mM IPA, SR of 1, 250 bar and a residence time of 6 s.

7.5.3 Effect of Oxidant Ratio

The effect of investigating different oxidant ratios in the presence of IPA is shown in Figure 72 based on IPA-free system that was discussed earlier in this chapter. Generally, the figure illustrates how adding just a ratio of 0.5 of IPA/ammonia positively enhanced the nitrogen removal in form of ammonia and TN with all oxidant ratios investigated. For example, at oxidant ratio of 1SR, the addition of 50% of stoichiometrically needed IPA improved the removal of ammonia and TN by 64% even though a relatively mild temperature of 450°C was used. Also, at oxidant ratios of 1.25 SR and 1.5 SR the presence of IPA made an enhancement in ammonia removal by 55% and 47%, respectively, and the improvement in TN removal was also around 60% and 50%, respectively when IPA added. Maximum ammonia removal of 84% with 1.5SR and in the presence of IPA and at 450°C indicated that it is highly possible to improve ammonia removal further by using more co-fuel and/or more oxidant and probably at lower temperatures.

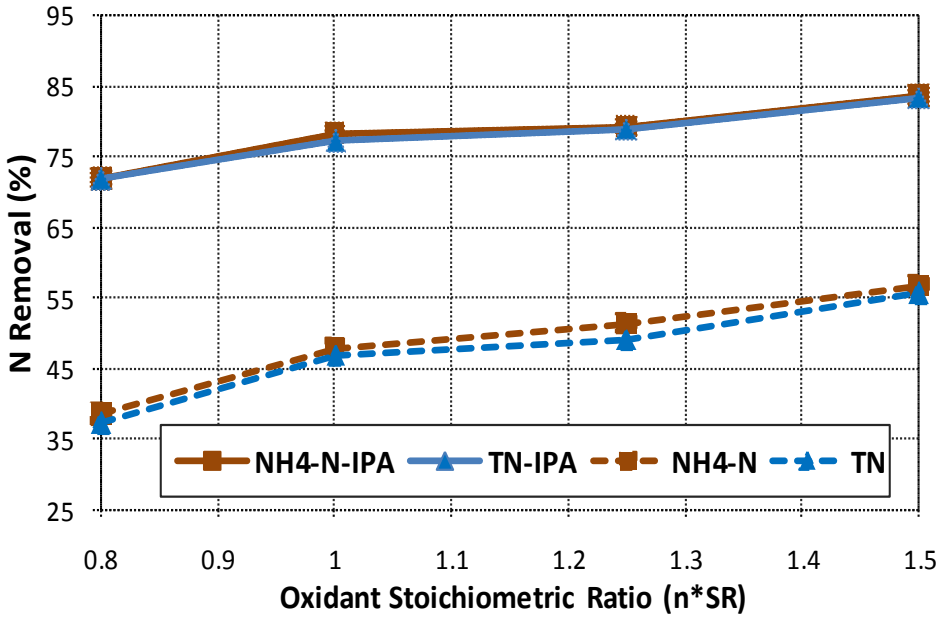


Figure 72: Effect of oxidant stoichiometric ratio on ammonia and TN removal at 10 mM ammonia, 5 mM IPA, 450°C, 250 bar and a residence time of 6 s.

Figure 73 shows the role of different oxidant ratios on nitrate and nitrite in the presence and absence of IPA. The figure shows clearly how IPA effectively kept nitrite at its lowest values, and considerably decreased nitrate formation with all oxidant ratios investigated. For example, the reduction in nitrate at oxidant ratio of 1SR was 60% when IPA was added with just a ratio of 0.5. The closure between TN and ammonia removals (as in Figure 72) especially in the presence of IPA during all oxidant ratios investigated shows the ability of IPA to effectively inhibit the generation of nitrate and nitrite and thus more of initial nitrogen would be converted to gaseous phase as a good destruction sign.

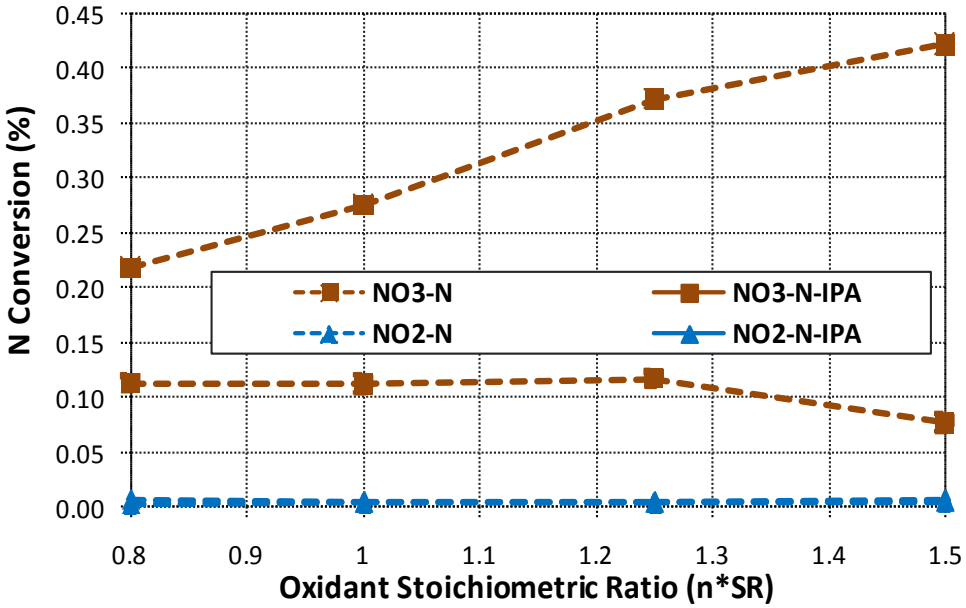


Figure 73: Effect of oxidant stoichiometric ratio on formation of nitrate and nitrite at 10 mM ammonia, 5 mM IPA, 450°C, 250 bar and a residence time of 6 s.

7.5.4 Effect of IPA Concentration Ratio

The effect of various ratios of IPA/ammonia was investigated on a wide range from zero till 4 by using 0, 1, 2.5, 5, 10, 20 and 40 mM of IPA and 10 mM of ammonia. Figure 74 shows the role of varying IPA/ammonia ratios at a temperature of 450°C, 1 SR and at a residence time of 6 seconds. The figure shows how adding IPA positively improved the nitrogen conversion in the form of ammonia and TN removals with studied ratios. This general trend was reported in several studies that showed that ammonia decomposition improves in the presence of other organic compounds (Cocero et al., 2000a, Cabeza et al., 2011, Shimoda et al., 2016). Generally, the removal of ammonia and TN increased with all ratios and with a dramatic increase at lower ratios such as from zero to 0.5. For instance, compared to non-IPA experiment, the removal of ammonia and TN improved from 47% at zero IPA to 57% at a ratio of 0.1 and to 78% at a ratio of 0.5 for IPA/ammonia, which represents an increase of 21% and 65%, respectively. Doubling

IPA ratio from the stoichiometric amount (IPA/ammonia ratio of 1) similarly improved both ammonia and TN removals by around 8%. Also, increasing IPA from the stoichiometric amount to the ratio of 4 made an improvement of 12% with maximum removal of 97.3% for both removals. These results are promising comparing to Cocero's work, who achieved complete ammonia removal and a TN removal >97% at optimum conditions of 600^{o}C, 1 SR, 43 seconds when IPA was used (Cocero et al., 2000a). She explained that the reduction in the operating temperature was due to the presence of IPA, where usually temperatures in excess of 650^{o}C are needed. Also, these results obtained in this work are in accordance with other findings that showed the removal of ammonia enhanced with higher ratios of co-fuels, such as methanol that was studied up to the ratio of 6 (Oe et al., 2007) and IPA that was investigated up to the ratio of 1.5 (Cabeza et al., 2014). Achieving a maximum ammonia removal of 97.3% at lower conditions of 450°C and stoichiometric oxidant indicates that complete ammonia oxidation is possible with higher IPA ratios, more oxidant and/or longer residence time or even a combination of all factors.

The significant role of IPA as enhancer in improving ammonia oxidation can be explained based on different mechanisms. First, the addition of IPA provides extra enthalpy content to the feed mixture where excess heat is produced through the exothermic oxidation reaction, and thus ammonia oxidation proceeds (Cocero et al., 2000a, Bermejo and Cocero 2008). For instance, it has been found that 1wt% IPA produced maximum temperature of 440^{o}C, while 5wt% IPA produced maximum temperature of 708^{o}C (Cabeza et al., 2011). Secondly, several authors showed that the presence of alcohols enhance free radicals (OH) generation improves ammonia destruction (Ploeger et al., 2007, Cabeza et al., 2014, Shimoda et al., 2016). Ploeger and co-workers added that reactive radicals have a positive effect on N distribution by producing N_2O that reacts with ammonia compared to pure ammonia oxidation. Shimoda and co-workers recently found that ammonia shares radical production with alcohol during co-oxidation, where

when OH radical supply stops (after complete methanol conversion) ammonia oxidation is maintained by N-containing species (HNO) that accelerates the conversion of the mixture to N_2O as a major product and to CO_2 (Shimoda et al., 2016). Thirdly, IPA as an alcohol is easily oxidised compound in which its oxidation would effectively accelerates the decomposition of other organic compounds (Ploeger et al., 2006a).

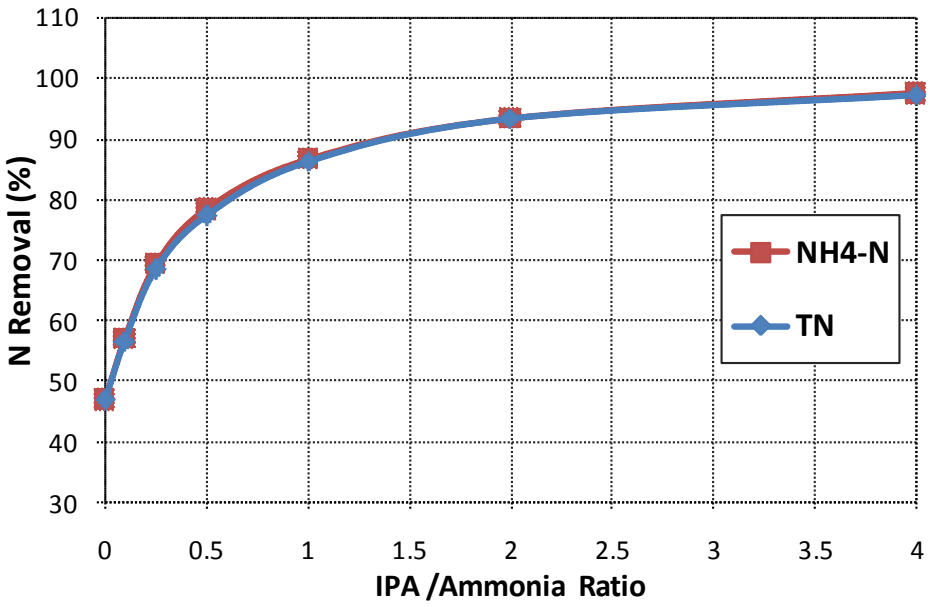


Figure 74: Effect of IPA/ammonia ratio on ammonia and TN removal at 10 mM ammonia, 450°C, 1SR, 250 bar and a residence time of 6 s.

Figure 75 shows the effect of IPA on nitrate and nitrite conversions. It was clear that the addition of IPA decreased the conversion of nitrogen into nitrate with all ratios studied, while nitrite was negligible. The same observation was reported in earlier study that showed increasing IPA inhibits the formation of nitrite, while nitrate formation decreased (Cocero et al., 2000a). The trend shows also that using higher IPA ratios would reduce nitrate as the most oxidative form of nitrogen in the liquid phase to its minimal levels.

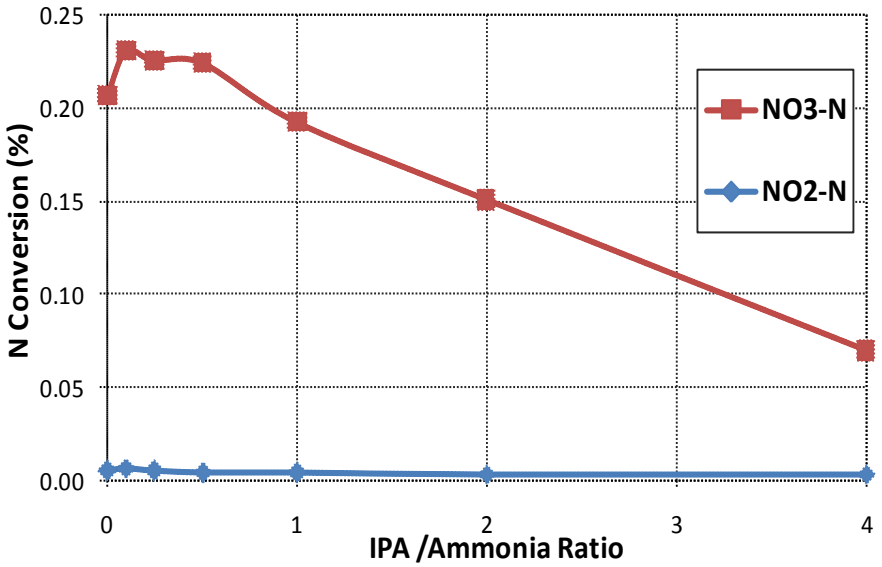


Figure 75: Effect of IPA/ammonia ratio on formation of nitrate and nitrite at 10 mM ammonia, 450°C, 1SR, 250 bar and a residence time of 6 s.

7.6 Summary

In this work, a range of temperatures were used to increase the removal of ammonia and nitrate, while nitrite was in trace amounts. Increasing oxygen also improved ammonia oxidation and nitrate formation, while nitrite level was negligible. Adding IPA also enhanced the role of temperature and oxygen to improve ammonia removal further and reducing nitrate. Using IPA as a novel approach showed a significant impact on ammonia removal, where maximum removal of 97.3% was achieved at a ratio of 4 and at milder temperature. Also, a significant reduction in nitrate was obtained, while nitrite was at its lowest level. Lastly, in addition to the destruction advantage of IPA, it has other economic features. For instance, the considerable reduction in the operating temperatures would minimise the cost of SCWO technology. Also, the generated excess heat from within the system in the presence of IPA during exothermic hydrothermal reactions could be used for preheating the feed using heat exchanger or recovered to produce hot steam through a boiler and then to generate electricity using steam turbines.

CHAPTER 8-CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The research work presented in this thesis covered both the general aim of increasing the collective knowledge of hydrothermal oxidation reactions in SCW and the specific objective of investigating the performance of SCWO technology in treating different dilute wastewaters containing three nitrogenous model compounds namely DMF, DBU and ammonia in the presence of IPA at different operating conditions. For this reason, a SCWO system was operated to obtain the experimental data presented and discussed in thesis. The obtained kinetic data was also used to develop global kinetics rate expressions for treated compounds. This included evaluating the effect of co-fuel on activation energy and operating temperatures. The following outlines the conclusions drawn from this research:

8.1.1 SCWO of DMF

A lab-scale tubular reactor was used for performing the research on SCWO of DMF-containing solutions. The system was used to investigate the destruction efficiency in the presence of IPA and kinetics at various operating conditions, such as temperature, oxidant ratios, organic concentrations and IPA ratios. Hydrolysis effect was found around 5% of TOC removal of DMF. Oxidation results showed that the temperature was the most influential variable affecting TOC removal. For instance, at minimum temperature of 400^{o}C the TOC removal was 88%, while near complete removal (99.2%) was observed at temperatures in excess of 525^{o}C, 250 bar, stoichiometric oxygen and 10 seconds of reaction time. The TOC conversion positively increased with increasing DMF feed concentration and oxidant ratio. Oxygen plays an important role in radical formation. Using different IPA concentration ratios significantly improved the

TOC removal. In general, the presence of IPA positively enhanced the role of all previous studied variables on TOC removal due to excess heat and free radicals generated. For instance, adding the stoichiometric amount of IPA improved the TOC removal by 8% to reach 88% at 400^{o}C with 10 mM DMF, 1SR and 10 seconds.

The yield of ammonia increased with the studied range of temperatures (400-525^{o}C) as ammonia always requires higher temperatures, thus its high concentration exceeded allowed disposal standards. This would require further treatment for ammonia by using higher IPA ratios or even by combining this with higher oxidant rations, higher temperatures or using catalyst. Combining SCWO with a biological step is also another option. DMF feed concentration and oxidant ratio increased the yield of ammonia which is mainly due to using low temperature (i.e. 400^{o}C). Using the stoichiometric oxidant was found to suppress the yields of ammonia, nitrite and nitrate. Also, using higher ratios of IPA concentrations reduced the yield of ammonia though lower range of temperatures was used in this work.

A kinetic analysis was carried out to quantitatively describe the effects of operating parameters on TOC removal (of DMF). A global rate expression, using Pseudo-first-order and integral assumptions, gave non-similar rate parameters indicating certain degree of oxygen dependency. From integral method, oxygen order was found to be 0.38 with Arrhenius activation energy (*Ea*) of (-22 kJ/mol) and a pre-exponential factor (*A*) of 2.4×10^5 $M^{-0.38}$ s^{-1} at 250 bar. This showed a huge reduction in the activation energy of DMF oxidation in the presence of IPA compared to IPA-free system (-140 kJ/mol), which facilitates for faster oxidation reaction with IPA as a novel approach. Also, it means the operating temperatures decreased due to IPA addition.

8.1.2 SCWO of DBU

Similar investigation was carried out using the same system to assess the destruction and kinetics of DBU oxidation in the presence of IPA at various operating conditions. Results showed that the TOC removal of DBU was lower than that of DMF, which is due to the fact that DBU has a complex structure. Hydrolysis effect was found around 5% of TOC removal of DBU. As with DMF, temperature showed a significant effect on DBU conversion. The results showed that near complete TOC removal (99.1%) can be achieved at 525^{o}C, 250 bar with stoichiometric oxidant and 10 seconds of residence times, while at 400^{o}C the TOC removal was 88%. The TOC conversion also improved with increasing DBU feed concentration and oxygen ratio. Using different IPA concentration ratios significantly improved the TOC removal. In general, the presence of IPA positively enhanced the role of all previous studied variables on TOC removal due to excess heat and free radicals generated. For instance, adding the stoichiometric amount of IPA improved the TOC removal from 99.1% to 99.4% at 525^{o}C, 5 mM DBU, 1SR and 10 seconds.

Increasing the temperature up to 525^{o}C increased ammonia production as higher temperatures are usually needed, while nitrite and nitrate were at minimal values. DBU concentration positively affected the yield of ammonia, while nitrite and nitrate were below 5%. On the other hand, ammonia yield was decreased with oxidant ratios. Also, using higher ratios of IPA concentrations effectively decreased the yield of ammonia in addition to nitrite and nitrate though lower range of temperatures was used in this work. Thus, presence of co-fuel forced the oxidation more towards the gaseous phase.

A kinetic analysis of DBU was performed using the same methods. From integral method and in the presence of IPA, the order of oxygen was 0.32 with Arrhenius activation energy (Ea)

of (- 21.96 kJ/mol) and a pre-exponential factor (*A*) of 41 $M^{-0.32}$ s^{-1} at 250 bar. This showed how IPA reduced the activation energy of DBU oxidation compared to IPA-free system (-25.7 kJ/mol), which facilitates for faster oxidation. Also, it means that operating temperatures can be reduced due to IPA addition.

This study proved that the oxidant has an influence on the oxidation reaction with an order of 0.38 and 0.32 with DMF and DBU respectively, which agrees with the literature.

8.1.3 SCWO of ammonia

Similar investigation was carried out using the same system to assess the destruction of ammonia in SCW in presence of IPA compared to non-IPA system at various conditions. Ammonia and total nitrogen (TN) removal increased with temperatures studied (400-550^{o}C), where the maximum removal for both was 58% at 550^{o}C, which indicates that high temperature always needed to effectively destroy ammonia. Therefore, further treatment is needed for ammonia by using higher temperatures or novel approaches such as using co-fuel or catalyst. Also, the yields of nitrite and nitrate were increased with this range of temperatures. Increasing oxidant ratios (0.8-1.5 SR) also increased the removal of ammonia and total nitrogen in addition to the yield of nitrate. However, it was obvious that using the stoichiometric amount of oxidant was ideal for better ammonia removal and less yields of nitrate and nitrite. The addition of stoichiometric IPA (5 mM) obviously enhanced the effects of previous variables as well. For instance, the removal of ammonia and TN was enhanced by around 50% to reach 84% at 550^{o}C, 1 SR and 5mM for IPA and ammonia. Also, its presence decreased the conversion of organic nitrogen towards nitrite and nitrate. Finally, higher ratios of IPA/ammonia (till ratio of 4) significantly improved the removal of ammonia and TN, in which a maximum removal of 97.4%

was achieved for both with IPA/ammonia ratio of 4 with 400^{o}C and 1SR. It was obvious that a complete ammonia removal could be achieved by using higher IPA ratios or even by a combination of IPA and mild temperatures than usually needed for ammonia. The conversion of nitrate was reduced by 60% with IPA/ammonia ratio of 4 indicating more decomposition towards nitrogen gas. Although ammonia has a simple structure, it showed its refractory nature over studied variables compared to other classes (DMF, DBU) where this is due to its tribble bond around N atom.

In general, the addition of co-fuel (IPA) obviously showed an efficiency to enhance the destruction of targeted compounds (DMF, DBU and ammonia) that represent broad classes of nitrogen-containing hydrocarbons that can be treated by SCWO technology. The efficiency of IPA was observed via the enhanced TOC and total nitrogen removal in addition to the reduction in the yields of ammonia, nitrite and nitrate. The positive role of IPA was due to the ability of co-fuel to generate extra heat and more free-radicals during its oxidation, and thus free radical mechanism dominates. Also, due to the rapid oxidation of IPA that accelerates the co-oxidation of associated compound in the feed solution.

Also, results showed the role of co-fuel (IPA) to reduce the operating temperatures, which is a very advantageous aspect that would help to effectively destroy organics (mainly ammonia due to its refractory nature, where nitrogen pathway requires higher temps than carbon pathway to be decomposed effectively) at lower temperatures than those normally needed.

8.2 Recommendations

The following recommendations are expected to benefit any future work based on observations from this study:

- Due to the positive effect of the auxiliary-fuel (IPA) on the conversions of treated compounds during this co-oxidation study, it is essential in any future further works to investigate higher concentrations of IPA coupled with a vast range of other variables in order to find the minimum optimised conditions for best organic removal and lowest ammonia yield. Co-fuel must be exploited due to its cost-effectiveness rather than consuming external heat source and due to its ability to minimise operating temperatures in order to further improve the destruction efficiency of the process. Besides, doing experiments it would be reasonable to make simulation and modelling studies to find optimum removal conditions for the SCWO of ammonia. Also, this sort of approach (adding IPA) would help to construct smaller PFR reactors in the future due to the fact that reducing the operating temperature would reduce total flow rate and thus the reactor can be smaller.

- Oxidising IPA resulted in producing extra heat due to its high calorific value, in which its recovery would enhance the process economic feasibility. Besides, destruction it is highly recommended in future to investigate the energy recovery especially on larger SCWO scales using different heating value wastes in order to extend this process efficiency and applicability. Moreover, lowering operating temperature aids to make SCWO a cost-effective method.

- Co-oxidation of two components applied in this study, where it is highly important to do further study on the co-oxidation of 3 or more components (IPA with different hetero atoms) to investigate the effect of IPA with a more complex feed and any possible technical challenges especially with the presence of IPA.
- Using co-fuels is highly recommended to treat real waste as treating such waste requires achieving high destruction regardless tracking specific component (kinetics, or pathways) where co-fuels accelerate the oxidation of TOC content.
- The treated DMF, DBU solutions in this work should include minimum amount of salt (inorganic) in their feeds, where there was no possible risk of salt precipitation. In case of ammonia solution it was expected that small traces of salt can be formed after oxidation reaction. However, using small diameter tubular reactor and high speed flow rate would minimize any risk of scaling and also no difficulty noticed during all runs. Also, due to the absence of any hetero-atom in all treated feeds the stainless steel 316 reactor showed reliability over 2 years to treat such feeds, in which nitrogen hetero-atom forms at the end nitrogen gas not acids. In future, any further study using this rig, the type of waste and its content should be considered to avoid any challenges or some parts must be replaced. Also, treating hetero-atom wastes with long term tests are essential on lab-scale to predict the reliability of SCWO system on large-scales.

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